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HEMICELLULOSES OF WHEAT STRAW[1]

BY G. A. ADAMS AND A. E. CASTAGNE

Abstract

Various hemicellulose fractions were extracted from wheat straw holocellulose (extractive and pectin free) by successive treatments with cold and hot water, 0.5%, 1.0%, and 2.0% potassium hydroxide and were recovered by precipitation with alcohol. Approximately 25% of the holocellulose material was removed, one half being in the hot water soluble fraction. The original holocellulose, the extracted residue, and the recovered fractions were analyzed for pentosan, uronic acid anhydride, acetyl, methoxyl, and ash content. In general, the more soluble fractions had a higher uronic acid and methoxyl content; the less soluble had a higher pentosan content and a more negative rotation $[\alpha]_D^{20}$. Intrinsic viscosity measurements indicated that all fractions had a degree of polymerization of 25–30. Hydrolysis of the main fraction yielded D-xylose, L-arabinose, D-glucose; in addition D-galactose was found in the water soluble fractions. Quantitative determinations of the sugars in the hydrolyzates showed that D-xylose predominated, with L-arabinose, D-glucose, and D-galactose (when present) in progressively smaller amounts. On hydrolysis all fractions yielded an acid-resistant uronic acid complex that contained D-xylose and a uronic acid tentatively identified as monomethoxyl galacturonic acid.

Introduction

Hemicelluloses may be extracted from plant materials by two general methods. The older and simpler of these employs direct extraction of the extractive-free plant tissue with dilute alkali. Precipitation of the hemicelluloses from the alkali by acids, alcohols, and other precipitants accomplishes a certain amount of fractionation. Various subfractionations and purification steps have been developed, and detailed summaries of these are reported in comprehensive reviews (19, 20). While much valuable information has been obtained with this approach, certain shortcomings have become apparent; a considerable proportion of the hemicelluloses are not extractable by dilute alkali except after removal of the lignin. In addition, a portion of the lignin that is simultaneously removed with the hemicellulose causes difficulties in the recovery and purification of the hemicellulose fractions.

The other general method, which is a recent development, makes use of holocellulose instead of the whole plant tissue as the starting material. Several satisfactory methods have been developed for the complete removal of lignin from plant material leaving a residue (holocellulose) that contains all the polysaccharide materials (27, 28, 29). Absence of the lignin permits ready

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extraction of hemicelluloses from the holocellulose. While it is believed that hemicelluloses are unchanged by the delignification processes, some are more readily soluble in water and mild alkali solutions after delignification, and a wider range of extraction conditions becomes possible (25). A study of the hemicelluloses from maple wood holocellulose by Mitchell and Ritter showed that approximately 20% of the holocellulose was extracted by water and dilute alkali (18). Chemical analyses of the fractions and molecular weight determination by end group assay indicated that a broad separation into different polysaccharides had occurred. Using a number of physical methods, Millet and Stamm found that hemicelluloses isolated with water and mild alkali treatments from aspen holocellulose showed only minor molecular weight differences (17). A similar extraction procedure applied to aspen holocellulose by Thomas indicated that chemical differences existed between the various fractions (25).

While this new approach to the study of hemicelluloses by the holocellulose route has been applied to a number of woods, no corresponding information appears to be available for annual plants and straws. The purpose of the present investigation was to extract the hemicelluloses of wheat straw holocellulose by means of mild solvents, and to determine the composition of the isolated fractions. Estimation of the approximate degree of polymerization of each fraction by viscosity measurements was also included. No attempt was made to obtain quantitative extraction of all the hemicellulose material; only the readily soluble material was sought by a combination of successive extractions and fractional precipitation.

Materials and Methods

Wheat straw holocellulose that had been prepared from mature straw by an acid chlorite method previously described (1) was used as starting material. Lignin determinations were made by the 72% sulphuric acid method (23). Pentosans were determined by distillation with 12% hydrochloric acid and the evolved furfural was measured by the bromine oxidation procedure described by Hughes and Acree (13). Corrections for furfural arising from uronic acid groups were applied, and pentosan values were calculated as xylan. Acetyl groups were determined by Clark's semimicro method (6). Uronic acid anhydride was estimated by a modification of the method of Dickson *et al.* (7) in which the carbon dioxide produced by decarboxylation was removed in a stream of carbon-dioxide-free nitrogen in an all glass apparatus. When only small amounts of material were available the micro method of Tracy was more convenient and equally satisfactory (26). The micro method of Somogyi was used for determination of reducing sugars (24). Detection and quantitative estimation of individual sugars in acid hydrolyzates of the various hemicelluloses were made by a combination of chromatographic techniques (11, 16, 21) which will be described in detail in the section dealing with separation and identification of sugar components. Moisture was determined by

drying to a constant weight at 100°C. in a vacuum oven unless otherwise stated; ash by incinerating at 550°C. Optical rotations of the hemicellulose fractions were measured at 1.0% concentration in 2.5% potassium hydroxide solution.

Experimental Procedures and Results

The investigation was developed in three steps: preparation of the hemicellulose fractions; chemical analyses of the isolated fractions and determination of their intrinsic viscosities; and hydrolysis of the hemicelluloses, followed by identification and quantitative determination of the component sugars.

Preparation of Hemicellulose Fractions

Preliminary Trials on Small Batch

Preliminary experiments were carried out on a 50 gm. lot of air-dried holocellulose to determine the amount of material extracted by successive treatments with water at 100°C., and 0.5%, 2.0%, 5.0%, 8.0% and 10.0% potassium hydroxide respectively, at 25°C. It was found desirable not to dry the residue after each extraction as the subsequent extraction period was prolonged owing to slow swelling of the cellulose. The alkaline extracts were neutralized with acetic acid, concentrated to a small volume, and precipitated by pouring into three volumes of 95% alcohol. The recovered hemicelluloses were washed repeatedly with warm alcohol, and then ether and finally dried to constant weight *in vacuo*. Table I records the conditions for extraction

TABLE I

Preliminary Extraction of Wheat Straw Holocellulose
(49.2 gm. of holocellulose (ash free))

Extracting agent	Vol. extracting agent, ml.	No. of extractions	Duration of each extraction, hr.	Weight of fraction (ash-free), gm.	Yield, % (ash-free)
Water at 100°C.	1000	3	4	5.28	10.7
Potassium hydroxide, 0.5%	800	2	3	4.27	8.7
Potassium hydroxide, 2.0%	600	2	3	2.23	4.5
Potassium hydroxide, 5.0%	600	2	3	2.12	4.3
Potassium hydroxide, 8.0%	600	2	2	1.10	2.2
Potassium hydroxide, 10.0%	500	2	2	1.21	2.4
			Residue:	31.00	63.0
				Accounted for:	95.8%

and the yield of each fraction. The most interesting result obtained was the unexpected solubility of about 11% of the holocellulose in hot water. Extraction with 0.5% potassium hydroxide, which is regarded as a mild treatment, removed a further 8.7%. The total amount of material removed by the extracting agents up to and including 5% potassium hydroxide totalled 28.2% of the holocellulose. This yield is in good agreement with a yield of approximately 29% when 5% potassium hydroxide was used as the sole extracting agent, reported earlier (2). These results indicated the feasibility of extracting wheat straw holocellulose with a succession of relatively mild solvents to yield appreciable amounts of hemicellulose materials.

On the basis of the foregoing preliminary experiments a further study was planned in which a 10-fold amount of holocellulose was used and a succession of even milder extracting agents employed. It was hoped that by using cold and hot water, 0.5%, 1.5%, and 2.0% potassium hydroxide successively, such extractions might preferentially separate polyuronide material from cellulosan fractions.

Extraction of a Large Batch of Holocellulose

The quantity of holocellulose used was 600 gm. (air dry weight). The extraction apparatus consisted of a 5 gal. glass jar fitted with a monel rake agitator travelling at 30 r.p.m. The jar was covered by a tight fitting lid containing ports for passage of nitrogen through the vessel. The jar was placed in a water bath and the temperature thermostatically controlled at 25°C. ± 0.5°. For hot water extractions a steam coil was installed in the bath.

Cold Water Extract

A cold water soluble fraction was prepared by extracting the holocellulose with 15 liters of distilled water at 25°C. for 120 hr. Microbial growth was prevented by the addition of 0.075 gm. of Dowcide 6 dissolved in 2 ml. of 0.1 *N* sodium hydroxide. The aqueous extract was removed by suction through a sintered glass filter stick (porosity C) immersed in the suspension and the residue was thoroughly washed with water. The extract and washings were slightly opalescent but contained no fine fibrous material. The solution was concentrated to about 2000 ml. in a laboratory flash evaporator at a temperature not exceeding 50°C. The pH of the concentrated extract was 6.82. Centrifuging the concentrated solution removed 0.19 gm. of material (Fraction 1) which was discarded and four volumes of alcohol were added slowly with stirring to the clarified solution. A white flocculent precipitate that came down was centrifuged off and dried by solvent exchange through alcohol and ether (Fraction 2). The supernatant solution from the recovery of Fraction 2 was concentrated to a small volume. On the further addition of alcohol another fraction was recovered (Fraction 3). Reconcentration of the supernatant solution and adjustment to pH 4.0 with hydrochloric acid followed by addition of four volumes of alcohol brought down another small precipitate

(Fraction 4). No further removal of hemicellulose being possible with alcohol, the solution was brought to pH 7.0 and evaporated to dryness at 45–50°C. (Fraction 5).

Hot Water Extract

A sufficient quantity of water was added to the wet residue from the previous extraction to bring the total volume to 15 liters. The water surrounding the extraction vessel was kept boiling vigorously. Four extraction periods of six hours each were made. The first extracts were brownish in color and had a pH of approximately 5.5. Efforts to control the pH at neutrality by the addition of alkali were only partially successful; relatively large amounts were required and contributed greatly to the difficulties of reducing the ash in the recovered fractions. The pH of the solution increased in successive extractions and color decreased until the final extract was only slightly colored. After thorough washing of the insoluble residue all the extracts were combined, adjusted to pH 6.0, and concentrated at 50°C. to a small volume. This solution was then dialyzed against running tap water for 48 hr. Total solids and ash in the solids were determined on an aliquot after dialysis was complete. Three volumes of alcohol were then added to the dialyzed solution and the white flocculent precipitate was removed and dried by solvent exchange through alcohol and ether (Fraction 6). The alcoholic supernatant solution was reconcentrated, five volumes of alcohol were added, and the precipitate was removed and dried (Fraction 7). A further small fraction was recovered by alcoholic precipitation after adjustment of the pH of the solution to 7.0 (Fraction 8). Since no further fractions could be obtained with alcohol the solution was taken to dryness under reduced pressure (Fraction 9).

Alkali Extract, 0.5% Potassium Hydroxide

The residue from the hot water extraction was made up to a total volume of 15 liters containing 0.5% potassium hydroxide. The extraction mixture was held at 25°C. and nitrogen was continuously passed over its surface. The pH of the solution was approximately 12.0. Three extraction periods of three hours each were employed. The combined extracts and washings were neutralized with hydrochloric acid and concentrated at 50°C. to 1/10 their volume. The concentrated solution was dialyzed successively in Visking casings against tap and distilled water until chloride-free (36 hr.). The solution was again concentrated and three volumes of alcohol were added with stirring. The heavy white precipitate was washed with alcohol and ether and dried (Fraction 10). Neither further addition of alcohol nor adjustment of pH caused further precipitations and the solution was taken to dryness under reduced pressure (Fraction 11).

Alkali Extraction, 1.0% Potassium Hydroxide

The extraction procedure was similar to that described above. Two extraction periods were used; one for six hours and another for 16 hr. The

extracted solutions were neutralized, concentrated, and dialyzed until salt-free. By addition of alcohol a flocculent precipitate was recovered (Fraction 12). A further small precipitate was obtained by a further addition of alcohol (Fraction 13). Evaporation of the alcoholic solution yielded a brown solid (Fraction 14).

Alkali Extract, 2.0% Potassium Hydroxide

The residue from the previous extraction treatment was subjected successively to a six- and a sixteen-hour extraction period with 2.0% potassium hydroxide. The residue was thoroughly washed with water and the extract and washings after neutralization reduced to about 1/10 their volume. Dialysis against tap water was carried out for 42 hr. After reconcentration of the dialyzed solution a small amount of brownish solid settled out and was centrifuged off (Fraction 15). By alcoholic precipitations a major fraction (Fraction 16) and a minor fraction (Fraction 17) were recovered and dried. The alcohol soluble portion was recovered as a brown powder (Fraction 18).

The cellulosic residue was washed with dilute acetic acid solution and then with water until free of acid. After three successive washes with alcohol the material was dried in warm air.

All major isolated hemicellulose fractions were purified by resolution in water or alkali and precipitation with alcohol. Some fractions on reprecipitation with alcohol tended to form gels which were difficult to recover and dry. Dehydration was finally achieved by adding the gels to large volumes of hot alcohol. Final drying after treatment with absolute alcohol and ether was carried out by desiccation under high vacuum. Fractions recovered by alcohol were all greyish powders; those taken to dryness were amorphous brown powders which were hygroscopic in air.

The yields of the various fractions are given in Table II. The total weight of the fractions recovered accounted for 94% of the original holocellulose; this recovery was satisfactory considering the number of operations involved. The fraction that was soluble in cold water amounted to approximately 2.4% of the holocellulose. The total amount of water-soluble material was about 14.7% and was considerably in excess of that found for hot water extraction in the preliminary experiment; this result was attributed to the exhaustive extraction employed. A total of 25.3% of the holocellulose was extracted by all treatments and of this approximately half was recovered from the hot water extract.

Analyses of Hemicellulose Fractions

The major fractions were analyzed for pentosan, uronic acid anhydride, methoxyl, and acetyl content and, in addition, their reducing power was determined. Optical rotations in alkali solution were also measured.

Many of the minor fractions were insufficient for complete analyses. However their composition was not regarded as a significant contribution to the

TABLE II

YIELD OF HEMICELLUOSE FRACTIONS FROM WHEAT STRAW HOLOCELLULOSE
(536.06 gm., moisture- and ash-free)

Fraction	Description of fraction	Weight (ash-free), gm.	% of original holocellulose	
	Cold water extract			
1	Material centrifuged from extract	0.1930	0.036	
2	First alcoholic precipitate	5.3317	0.995	
3	Second alcoholic precipitate	3.3576	0.626	
4	Alcoholic precipitate at pH 4.0	0.4694	0.083	
2*a*	Insoluble material from purification of 2	0.0852	0.016	
5	Alcohol soluble residue	3.3134	0.618	
				2.37
	Hot water extract			
6	First alcoholic precipitate	55.6728	10.38	
6*a*	Insoluble material from purification of 7	0.8276	0.154	
7	Second alcoholic precipitate	3.7712	0.704	
8	Alcoholic precipitate at pH 4.0	1.2874	0.240	
9	Alcohol soluble residue	4.4361	0.826	
				12.30
	0.5% KOH extract			
10	First alcoholic precipitate	28.0000	5.220	
11	Alcohol soluble residue	1.6434	0.306	
				5.53
	1.0% KOH extract			
12	First alcoholic precipitate	8.8218	1.645	
13	Second alcoholic precipitate	0.0538	0.010	
14	Alcohol soluble residue	0.8225	0.153	
				1.81
	2% KOH extract			
15*	Insoluble material appearing on dialysis	.....	.....	
16	First alcoholic precipitate	16.2130	3.03	
17	Second alcoholic precipitate	0.3233	0.062	
18	Alcohol soluble material	0.9653	0.179	
				3.261
	Residue	368.59	68.70	
	Total yield recovered:		94.0%	

**Sample lost.*

over-all interpretation of the hemicellulose components of holocellulose. The results of the analyses are given in Table III.

The main fractions Nos. 12 and 16 had optical rotations similar to those generally reported for plant and wood hemicelluloses high in xylan content (14, 18). The high negative rotation is indicative of β configuration in the molecule. The other fractions had rotations somewhat lower owing to a lower pentosan content. The low rotations of the alcohol soluble fractions indicated a low hemicellulose content—an observation confirmed by the small

TABLE III

COMPOSITION OF HEMICELLULOSE FRACTIONS
(All values calculated on a moisture-free basis)

	Fraction No.	Description of fraction	$[\alpha]_D^{20}$	Reducing power*	Pentosan, %	Uronic acid anhydride, %	Methoxyl, %	Acetyl, %
Water at 25°C.	2	First alcoholic precipitate	−72.0	6.34	64.6	8.84	1.30	2.92
	3	Second alcoholic precipitate	−58.6	11.4	57.4	8.36	2.05	2.64
	5	Alcohol soluble	−11.0	25.9	13.4	8.16	10.30	1.73
Water at 100°C.	6	First alcoholic precipitate	−67.0	6.3	64.7	8.44	3.50	3.17
	7	Second alcoholic precipitate	−44.0	18.8	48.4	7.84	5.21	4.25
	9	Alcohol soluble	−29.6	42.1	15.0	5.84	7.70	2.01
Potassium hydroxide, 0.5%	10	Alcoholic precipitate	−69.1	1.4	79.9	10.40	3.48	.00
	11	Alcohol soluble	+2.2	12.9	2.43	3.00	15.00	.00
Potassium hydroxide, 1.0%	12	Alcoholic precipitate	−90.0	1.3	82.0	5.00	0.95	.00
	14	Alcohol soluble	−12.5	11.2	8.0	4.88	10.46	.00
Potassium hydroxide, 2.0%	16	Alcoholic precipitate	−92.0	2.0	85.0	4.72	1.08	.00
	18	Alcohol soluble	+28.0	11.7	—	—	12.28	.00
		Holocellulose residue			17.5	2.04	0.14	

**Expressed as milliliters of 0.05N thiosulphate per gram of hemicellulose.*

pentosan content found in all these materials. The uronic acid anhydride content of the more easily soluble fractions was considerably higher than those removed by the 1 and 2% alkali. This result is in agreement with the general behavior of polyuronide hemicelluloses whose polar carboxyl groups render them more readily soluble in aqueous solution. In general, alkali of increasing strength extracted material successively higher in pentosan and lower in uronic acid anhydride. Apparently the fractionation procedure effected partial separation of the polyuronide and cellulosan components. The molar ratio, methoxyl : uronic acid anhydride was approximately unity for Fractions 2, 12, and 16, and indicated the presence of monomethoxyhexuronic acids in the hemicellulose molecules. In the other fractions, the methoxyl contents were high and excessively so in the alcohol soluble material. The source of the excess methoxyl may have been lignin residues in the holocellulose since the lignin content of the holocellulose decreased from 1.56% to 0.60% after the various extractions. No acetyl groups were found in the fractions prepared by alkali extraction because of the saponifying action of the alkali.

Intrinsic Viscosity Determinations

For viscosity measurements the five main hemicellulose fractions were fully acetylated by the method of Carson and MacLay (5). Solutions containing 0.5% of the acetylated material were made up in chloroform from which 0.25%, 0.125%, and 0.0625% solutions were also prepared by dilution of the original solution. Flow times were measured on freshly prepared solutions in an Ostwald–Cannon–Fenske type viscometer (ASTM 50) in a water bath maintained at 25°C. ± 0.02°C. All solutions were drawn into the viscometer through a thin cotton filter to remove stray dust particles. Flow time measurements were made in triplicate or until agreement to ± 0.1 sec. was obtained. Reduced viscosity values were calculated by substitution in the expression

$$\frac{T - T_0}{T_0 C}$$

where T = flow time of solution in seconds,
T_0 = flow time of solvent in seconds,
C = concentration of solute in grams per 1000 ml. of solution.

A plot of reduced viscosity against concentration of solution permitted extrapolation of the curve to zero concentration. The plots of $\eta\ sp/c$ against C were found to be straight lines for all fractions at the concentrations used, and the intercept of the curve on the ordinate gave the intrinsic viscosity $[\eta]$.

The intrinsic viscosities of the various acetylated fractions in chloroform were as follows:

	$[\eta]$
Fraction No. 2—Hemicellulose soluble in cold water	0.030
Fraction No. 6—Hemicellulose soluble in hot water	0.028
Fraction No. 10—Hemicellulose soluble in 0.5% alkali	0.027
Fraction No. 12—Hemicellulose soluble in 1.0% alkali	0.033
Fraction No. 16—Hemicellulose soluble in 2.0% alkali	0.026

The similarity of the [η] values suggested that the degree of polymerization (P) of the various fractions was of the same general order. Such a conclusion was based on values obtained by substitution in Staudinger's equation,

$$\eta\ sp/c = Km\ P.$$

When Km was assigned the value of 11×10^{-4}, the degree of polymerization of the various fractions was in the range of 25–30. The Km value of 11×10^{-4} has been used by Millet and Stamm for calculating molecular weights of acetylated hemicellulose fractions previously extracted from aspen holocellulose (17). Until the Km factor has been determined by suitable methods for acetylated hemicellulosic materials in chloroform, the value 11×10^{-4} must be used with considerable reservation. The low solubility of acetylated hemicelluloses in organic solvents—an observation made by other investigators (5) leads to difficulties in obtaining a molecularly dispersed solution for viscosity determinations. A number of organic solvents including chloroform, pyridine, formamide, methylene chloride, tetrachloroethane (alone and mixed with ethanol) were investigated; of these, chloroform proved the most satisfactory. All acetylated fractions appeared to give molecularly dispersed solutions in chloroform except No. 16, which was slightly opalescent; the rather low viscosity of the latter may be attributed to lack of complete molecular dispersion. Some viscosity determinations of the original fractions in 2% sodium hydroxide yielded [η] values of the same general order as for the acetylated material. However, the value for Fraction No. 16 was found to have the highest viscosity of all in alkali. Only limited studies were made using 2% alkali since concentration of the fractions above 0.25% in this solvent deviated from a straight line when $\eta\ sp/c$ was plotted against C.

Hydrolysis of Hemicellulose Fractions

Each of the main hemicellulose fractions was hydrolyzed by the following general procedure: approximately 0.5 gm. of the material was added to 50 ml. of 3% sulphuric acid (v/v) and the mixture heated in a boiling water bath under reflux. Most of the fractions were readily dispersed after a short period of heating except for a small residue which persisted throughout the hydrolysis period. The course of the hydrolysis was followed by change in optical rotation and total reducing power of the solution. The rotations changed from strongly negative to slightly positive readings after three to six hours' heating. The reducing power for most fractions reached their maximum in the six to nine hour period. After 12 hr. heating the reducing power began to decrease and the appearance of a brownish color indicated some sugar destruction. All insoluble residues were removed, washed with water, alcohol and ether, then dried and weighed. The amounts of the unhydrolyzed residues constituted about 4–5% of the original material. The acid hydrolyzates were neutralized by the addition of a calculated amount of barium carbonate. Vigorous stirring and heating to 40°C. precluded the addition of an excess of the carbonate. The supernatant solution was recovered by centrifuging and

the barium sulphate precipitate was repeatedly washed with warm water. The solution and washings were decolorized and clarified by heating with 0.5-gm. quantities of Norite and Supercel respectively. After evaporation under reduced pressure the solution was poured into five volumes of alcohol. The solution was centrifuged and the precipitate of barium uronate dried with alcohol and ether and set aside for examination later. The alcoholic supernatant solution was concentrated to a thick syrup, taken up in water, and treated again with alcohol to remove further traces of barium uronate. After freeing from alcohol the syrup was taken up in 50 ml. of water for chromatographic examination for sugars.

Paper Chromatography of Sugars

The component sugars of each hydrolyzate were detected by a descending paper chromatography technique described by Partridge (21). The solvent system was ethyl acetate–water–pyridine (2:2:1) and the developing indicator was aniline phthalate. All chromatograms were run for 16–22 hr. in a sealed glass jar. In qualitative tests the reference sugars were D-xylose, L-arabinose, D-glucose, D-galactose, D-rhamnose, and D-mannose. After detection of the sugars in the hydrolyzates, the amounts of each were determined quantitatively by a procedure similar to that described by Hawthorne (11). The various individual sugar components were separated by filter paper chromatography from known volumes of the acid hydrolyzates. Known sugars on the same paper strip served to locate the exact region of the hydrolyzate spots. The spots were cut out, extracted with water and the reducing power of the extracts determined. These values were then readily calculated in terms of milligrams of the appropriate sugar. Xylose, arabinose, and glucose were found in all fractions and in addition galactose occurred in the water soluble fractions. The amounts of each sugar in the various hemicellulose fractions are shown in Table IV.

TABLE IV

SUGAR CONSTITUENTS OF HEMICELLULOSES, %

Fraction No.	Xylose	Arabinose	Glucose	Galactose
2	59.2	8.6	9.8	4.8
3	56.6	9.8	4.5	1.6
5	10.3	4.0	3.1	Nil
6	62.4	12.15	5.3	1.1
7	49.4	9.55	3.1	Nil
9	28.6	7.8	2.6	Nil
10	72.2	8.5	4.3	Nil
11	trace	trace	Nil	Nil
12	85.0	9.0	3.8	Nil
16	86.2	9.6	4.2	Nil

Identification of Sugars

The individual sugars detected by chromatography were identified by isolation and measurement of physical constants of either the sugar or derivatives. The sugar solutions from the foregoing experiments were pooled for the following tests. The aqueous sugar solution was evaporated to a thick syrup at 45°C. and the water removed by repeated distillation with absolute ethanol. The syrup was taken up in hot glacial acetic acid and on standing deposited a crop of D-xylose, which on recrystallization had an m.p. of 145–146°C., unchanged on admixture with an authentic sample, and $[\alpha]_D^{20} = +19.8$. After removal of most of the xylose by crystallization, L-arabinose was recovered as its benzoyl hydrazone, m.p. 185°C., unchanged on admixture with an authentic sample, and $[\alpha]_D^{20} = +23.8$. After removal of the excess benzoyl hydrazine by treatment with formaldehyde and extraction with ethyl ether, the addition of phenylmethylhydrazine yielded the crystalline phenylmethylhydrazone of D-galactose, m.p. and mixed m.p. 182–183°C. (12). On treatment of the remaining solution with phenylhydrazine an osazone was isolated that was converted to glucose phenylosatriazole (10), m.p. and mixed m.p. 195–196°C. Further proof of the presence of glucose was obtained by selective fermentation. A species of *Torula utilis* known to ferment only glucose was used to ferment a sample of the acid hydrolyzate. The fermented solution was chromatographed on the same paper strip as the unfermented solution and showed clearly that glucose was completely absent in the fermented solution. Arabinose, xylose, and galactose were unaffected.

Barium Uronate Salt

The barium salt precipitated by alcohol from the hemicellulose hydrolyzates was purified by repeated solution in water and reprecipitation with alcohol. The final product was recovered as a fine white powder with the following analysis: barium, 24.6%; methoxyl, 4.3%; uronic acid anhydride, 23.4. A molar ratio of methoxyl to uronic acid groups of 1.04 was evidence of a monomethoxyl hexuronic acid. The barium salt gave a strong napthoresorcinol test for uronic acid. Specific color tests for glucuronic and galacturonic acid (8, 9), were interfered with by a pentose sugar in the uronic acid complex. The presence of a pentose sugar was shown by a strongly positive Tollens orcinol test.

The barium uronate salt was hydrolyzed by sealing 123 mgm. in a glass tube with 2 ml. of 4% sulphuric acid (v/v) and heating at 120°C. for 8½ hr. The hydrolyzate was neutralized with barium carbonate, filtered, and clarified with charcoal. The solution was then chromatographed using as references substances free glucuronic acid, glucuronic acid lactone, and galacturonic acid as well as xylose, arabinose, glucose, and galactose. Xylose was clearly demonstrated as the only sugar present and must have been freed on hydrolysis, as the original barium uronate salt contained no free xylose. The spots of the reference free glucuronic and galacturonic acids showed slow migration and were approximately equidistant from the starting line; glucuronic acid lactone

formed a fast moving spot near the bottom of the paper after 16 hr. The unknown barium uronate solution produced a spot in the same position as the free uronic acids but there was no trace of glucuronic acid lactone. Positive identification of the unknown from its position was not possible but the shape of this spot resembled very closely that of the known free galacturinic acid. Insufficient material was available to give a trustworthy mucic acid test. It was possible to conclude that the hemicelluloses contained a uronic acid complex in which the sugar unit was D-xylose and the uronic acid possibly galacturonic.

Discussion

Hemicelluloses as usually prepared by alkali extraction of plant tissue are composed of both polyuronides and cellulosans (19). The cellulosans, being an integral part of the plant cellulose, are more difficult to extract than the polyuronides. The ready preparation of holocellulose provides a source of both materials free from the interfering action of lignin, and several investigators have attempted recently to fractionate the holocellulose with solvents considerably milder than those previously used (17, 18, 25). The general conclusion drawn from these studies has been that the isolated fractions show systematic trends in chemical composition that are related to solubility. In the present investigation on the fractionation of wheat holocellulose, five main fractions were isolated by relatively mild treatments. The main water soluble fractions were characterized, in general, by a higher uronic acid anhydride and methoxyl content than the alkali soluble materials; the latter, however, contained a considerably higher pentosan content. This result was indicative of a partial fractionation into polyuronides and cellulosan although the inclusion of approximately 5% uronic acid anhydride in the alkali soluble fractions showed that the separation was by no means sharp. The heterogeneity of hemicellulose material made the usual methods of fractionation empirical and it is doubtful if separate entities can be prepared by these techniques.

From considerations of solubility, the most soluble fractions would be expected to contain the short chain material. However, as Ritter has pointed out, a long chain hemicellulose containing uronic acid groups may have the same solubility as a short chain hemicellulose with no acid groups (22). It is possible then to have long and short chain material precipitated together from the extract. The intrinsic viscosity values were approximately of the same order for all fractions. The apparent chain lengths did not appear to show the variations expected on the basis of solubility although as pointed out earlier the calculation of the *DP* is restricted by inadequate data on the *Km* factor.

Millet and Stamm found that successive hemicellulose fractions isolated from aspen holocellulose had approximately the same molecular weights (*ca.* 8000) as determined by the viscosity method (17). End group methods (iodine number) by the same authors gave quite different results. Relatively wide variations in minimum molecular weights of maple wood hemicelluloses

extracted by water and dilute alkali were found by Mitchell and Ritter (18). However, chemical methods for molecular weight estimation involving reducing groups are known to be unreliable, especially if the material has been treated with alkali in air.

All hemicellulose fractions isolated were shown to contain xylose, arabinose, and glucose, with xylose predominating. Galactose was found only in the water soluble fractions. It is not known whether or not the hexosans are chemically combined with the pentosan material. Evidence put forward by Carson and MacLay (5) and Anderson *et al.* (3) supports the view that the hexosan and pentosan materials are chemically linked. In another method of separation studied in this laboratory for fractionating wheat straw hemicelluloses, a small constant amount of glucose and galactose was found associated with the pentosans in all fractions (4). The recent work of Isherwood (15) on pear cell wall polysaccharides using electrophoretic methods has indicated that polysaccharides generally regarded as complex may be a mixture of simple polymers containing only a single sugar each. At present, attempts are being made to resolve the hot water soluble hemicellulose (fraction No. 6) into single units by fractional precipitation of the acetylated material from chloroform solution.

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HYDROGEN PEROXIDE AND ITS ANALOGUES

II. PHASE EQUILIBRIUM IN THE SYSTEM HYDROGEN PEROXIDE – WATER[1]

By William T. Foley[2] and Paul A. Giguère

Abstract

A precision freezing point apparatus with platinum resistance thermometer was used to investigate the system hydrogen peroxide – water over the whole concentration range. The freezing point of the purest sample of hydrogen peroxide obtained by repeated fractional crystallizations of a large quantity of 99.6% pure solution was found to be −0.461°C.; that of the dihydrate was −52.10°C. The two eutectics occur at concentrations of 45.2% and 61.2% H_2O_2 and at temperatures of −52.4° and −56.5°C. respectively. Contrary to what has been reported previously, water and hydrogen peroxide do not form solid solutions together. This was proved conclusively by applying the technique of radioactive tracers to the 'wet residue' method of Schreinemakers.

The purpose of this investigation was threefold. First, to redetermine the freezing point of pure hydrogen peroxide, with greater accuracy than heretofore (3). Second, to settle the question of solid solutions in the system hydrogen peroxide – water (6). Third, to use freezing point measurements for evaluating the degree of purity of very concentrated hydrogen peroxide. Indeed, the usual chemical methods of analysis are of little use for that purpose since the remaining traces of water cannot be determined directly (4). Other physical methods investigated so far are either not sensitive enough or subject to errors due to spontaneous decomposition. These three objectives are closely interconnected; for instance, the existence of solid solutions would render determinations of freezing point rather problematic. At the same time it could rule out the possibility of using this method for accurate analysis.

Experimental Methods and Results

Freezing Points

An apparatus similar to that originated by Mair (12) and perfected subsequently by Rossini and his collaborators (7, 13, 20) at the National Bureau of Standards was constructed for this purpose. The double-walled, silvered freezing tube had an internal diameter of 3 cm. and the rate of heat transfer was controlled by adjusting the pressure inside the annular space. The cold head was provided by a large Dewar flask filled with dry ice and acetone. The problem of stirring the sample presented some experimental difficulties since most materials catalyze the decomposition of hydrogen peroxide. Stirrers made of glass rods were too fragile. Aluminum or highly polished stainless steel has been recommended as suitable for this purpose (18); the latter was selected because of its greater strength. The stirrer was in the form of a double helix fashioned

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by winding a 1/16 in. rod first downwards on a wooden mandrel 9/16 in. diameter and then upwards on a cylinder 11/16 in. diameter over a 3 in. length. The stirrer was polished electrolytically (19) by making it the anode in a bath of 47% glycerol, 42% sirupy phosphoric acid, and 11% water. Electrolysis was carried out with a cathode of the same material in a bath at 125°C. with a current density of 0.2 amp. per sq. in. After a few trials, surfaces could be obtained that were completely inactive towards hydrogen peroxide. The stirrer was actuated by a windshield wiper type of motor with a reciprocating stroke of $2\frac{1}{2}$ in. at the rate of two strokes per second. The apparatus was completed by a cork stopper covered with aluminum foil and through which the thermometer and stirrer were inserted, the latter guided by a length of glass tubing; two other inlets were provided, one for introducing crystals for seeding the sample and the other for blowing a stream of well dried air. This last precaution was necessary because concentrated hydrogen peroxide is very hygroscopic at low temperature.

The first few runs were made with a Beckmann thermometer, but it was soon realized that the time–temperature curves could not be followed long enough to give significant results, especially with the less concentrated solutions. A platinum resistance thermometer (Leeds and Northrup, type 8163) certified by the National Bureau of Standards was therefore used in conjunction with a Mueller bridge. The bridge was calibrated according to regular practice (15) against a 10 ohm Standard kept at 20.0°C. The ice point of the thermometer was determined after the method of Busse (2). Its resistance at 0°C. was 25.5188 international ohms. This value was again checked when the investigation was completed and perfect agreement obtained. The degree of reproducibility obtainable with this method and apparatus may be judged from the results in Table I.

TABLE I

TYPICAL RESULTS OF FREEZING POINT DETERMINATIONS

Run No.	Weight % H_2O_2	Freezing point, °C.
16	99.5$_8$	−0.869
17	99.5$_8$	−0.873
18	99.5$_8$	−0.876
33	99.7$_4$	−0.655
34	99.7$_4$	−0.655

Runs No. 33 and 34 were carried out on the same day, Nos. 16, 17, and 18 on successive days, the solution being kept at room temperature in the meantime. Although there was no evidence of streamers in the liquid it is likely that the slight drift in the freezing point is due to actual decomposition. Calculations show that the variation corresponds to a concentration change of 0.003% per day, which is far beyond the limit of accuracy of volumetric analysis in that concentration range. These observations confirm, therefore, the

superiority of freezing point measurement over chemical analysis for determining the purity of concentrated hydrogen peroxide.

The hydrogen peroxide used for these measurements was Becco's 90% solution. By fractional distillation through a 60 cm. glass column packed with Pyrex helices the concentration could easily be brought up to around 99.6%. Then it was subjected to fractional crystallization, the progress of concentration being followed by means of freezing point determinations. To be effective this last operation had to be carried out with great care. The solution to be concentrated was cooled in a stoppered flask and crystallization induced by seeding. It was then kept at −2°C. for several hours with occasional shaking. Then the two phases were separated by means of the device shown in Fig. 1. Flask *A* containing the partly frozen solution was inverted by rotating the connecting tube about ground joint *J*. By applying suction over flask *B* the liquid was filtered through the fritted glass plate. Thus any dilution from condensation of atmospheric moisture was avoided.

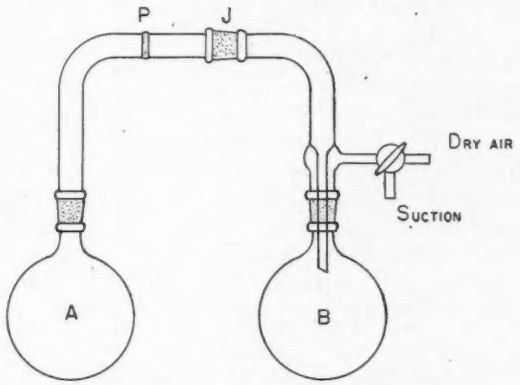

FIG. 1. *Apparatus for concentrating hydrogen peroxide by fractional crystallization.*

About 70 gm. of liquid was needed for a freezing point determination. In one series of determinations about 3 lb. of a 99.6% solution was recrystallized a number of times. The freezing point was measured when about two pounds was left and four times thereafter with at least two fractional crystallizations between successive measurements. The results shown in Table II are believed to be the most reliable to date. The measurements were carried out immediately after a recrystallization except in the case of Run No. 40 where the sample was left standing overnight, which may explain the slight discrepancy.

A second set of experiments was made starting with 1 lb. of concentrated solution, so that only three determinations could be made. The refractive index of the sample used for Run 39 was 1.40669 at 25°C., in perfect agreement with the latest results from this laboratory (4).

TABLE II

FREEZING POINT OF PURE HYDROGEN PEROXIDE

Run No.	Weight % H_2O_2*	Freezing point, °C.
1st series		
29	99.7_9	−0.479
31	99.9_5	−0.465
38	100.0_2	−0.461
39	99.9_7	−0.461
40	99.9_3	−0.469
2nd series		
30	99.8_2	−0.500
32	99.9_3	−0.492
37	99.9_0	−0.461

* *From volumetric analyses.*

The method of W. P. White (21) for calculating the freezing point at zero impurity from time–temperature curves was applied to the above determinations assuming that traces of water were the only contaminant in the peroxide. The calculations were based on the portion of the cooling curve where from 1/10 to 1/3 of the sample was frozen. The results, summarized in Table III, are rather inconsistent as a whole, apparently owing to the fact that the system was very sluggish in reaching equilibrium. Other investigators (1) have reported that in the case of hydrocarbons equilibrium is attained within four or five minutes. In associated liquids, however, the high viscosity slows down diffusion considerably and this may lead to spurious results.

TABLE III

CALCULATED FREEZING POINT AT ZERO IMPURITY

Run No.	Fraction frozen	Temperature, °C.	Freezing point, °C. (at zero impurity)
30	1/10	−0.508	−0.428
,,	1/5	−0.517	−0.432
31	1/5	−0.469	−0.448
,,	1/3	−0.474	−0.447
32	1/10	−0.495	−0.468
,,	1/5	−0.498	−0.468
,,	1/4	−0.501	−0.465
37	1/5	−0.470	−0.425
,,	1/4	−0.472	−0.428
39	1/10	−0.465	−0.425
,,	1/5	−0.469	−0.429
40	1/5	−0.473	−0.451

Using the same apparatus and technique the freezing point curve of the system hydrogen peroxide – water was re-examined. Some twenty measurements covering the entire concentration range were carried out, particular attention being paid to the region between 40 and 60%. On the whole the results (Table IV) agree fairly well with those of previous investigators (6, 9, 11) except for the freezing point of the addition compound $H_2O_2.2H_2O$. A comparison of the various values for this latter quantity and the co-ordinates of the two eutectic points is shown in Table V.

TABLE IV

FREEZING POINT OF HYDROGEN PEROXIDE SOLUTIONS

Run No.	Weight % H_2O_2	Freezing point, °C.
43	3.40	-1.99_4
42	5.81	-3.49_5
44	9.40	-5.93_8
52	19.6_5	-14.3_1
51	28.1_5	-23.2_8
53	39.1_4	-39.9_7
55	44.6_5	-51.0_4
60	46.8_0	-52.1_6
62	48.5_1	-51.9_9
56	48.5_7	-52.1_0
59	48.6_4	-52.1_0
61	51.9_2	-52.4_0
50	57.7_7	-54.5_3
58	60.3_1	-56.1_2
54	70.9_4	-38.8_4
48	81.1_2	-23.0_1
46	91.0_4	-10.2_1
47	95.3_3	-5.35_6
45	95.6_8	-5.05_1
27	97.5_6	-3.18_2

TABLE V

COMPOUND AND EUTECTICS

1st eutectic		Compound		2nd eutectic		Authors
Weight % H_2O_2	Temp., °C.	Weight % H_2O_2	Temp., °C.	Weight % H_2O_2	Temp., °C.	
45	−53	48.6	−51	59	−56	Maass and Herzberg
46	−51.5	,,	−50.3	60	−56.5	Giguère and Maass
45.8	−52.5	,,	−50.3	59.0	−55.5	Kubaschewski and Weber
45.2	−52.4	,,	−52.10	61.2	−56.5	This work

Solid Solutions

The so-called 'wet-residue' method of Schreinemakers (17) was applied using potassium chloride for the third component. Indeed, it is soluble in both liquids and is easily determined; in addition it does not decompose hydrogen peroxide. Two experiments were done with dilute peroxide solutions and two with concentrated solutions. The ternary mixtures were placed in a constant temper-

ature bath (5) and crystallization was induced by seeding at a few degrees below the freezing point. Temperature was gradually lowered by about 10 degrees so that a good portion of the sample was solidified. After remaining at least 10 hr. at that temperature the two phases were separated as thoroughly as possible by siphoning the liquid through a filter stick. Both phases were then analyzed, potassium chloride being determined gravimetrically with silver nitrate, and hydrogen peroxide, by the usual titration with permanganate. The results of Table VI were plotted on a tricoördinate graph; the corresponding lines when extrapolated passed exactly through the apex in all four cases, thereby indicating that no solid solution existed on either side of the phase diagram.

TABLE VI

RESULTS OF THE 'WET RESIDUE' METHOD WITH POTASSIUM CHLORIDE

Filtration temperature, °C.	% Composition of mother liquor			% Composition of wet solid		
	KCl	H_2O_2	H_2O	KCl	H_2O_2	H_2O
−15	7.09	17.64	75.3	4.62	10.78	84.6
−15	11.38	15.49	73.13	7.16	9.98	82.9
−23.8	4.48	79.3	16.2	1.24	94.6_4	4.1_2
−23.8	2.12	79.9_5	17.9_3	0.93	93.7_8	5.9_2

An objection to the above method is that addition of a third component in the large amounts needed for significant analysis may disturb considerably the normal equilibrium between the two major components. A solution of this difficulty in the present case was discovered in the use of radioactive tracers. Because of the very minute quantity needed there can be no disturbing effect of such a third component; yet the techniques of radioactivity measurements and the availability of concentrated isotopes result in an accuracy considerably greater than that of conventional chemical analysis. Radioactive phosphorus P^{32} in the form of potassium dihydrogen phosphate was used for this purpose as it fulfilled a number of desirable conditions: solubility in both water and hydrogen peroxide; inertness towards the latter; only one type of particles (β) emitted, and with sufficient energy (1.7 Mev.), to allow use of thin walled glass counters; half life of the right order of magnitude (14.3 days) for the proposed experiments and at the same time presenting no serious problem of contamination. The isotope was obtained from the Atomic Energy Project of the National Research Council at Chalk River. The original sample weighing 0.028 gm. had an activity of 0.95 millicurie when shipped. It was diluted a 100-fold and an amount added to give a concentration of 0.00025 gm. per liter of peroxide solution.

Two determinations were made, one with a 7% and one with a 95% solution of hydrogen peroxide. The phase separation was effected at −10°C. as described above and the activity measured with a Geiger–Mueller counter (Tracerlab No. TGC-5). The plateau of this counter had a slope of the order of 5% per 100 volts; starting voltage, 825 v. The operating voltage was kept at 900 v.±

0.1% by means of a stabilized power supply. The Geiger tube was mounted in an inverted position so that a test tube of appropriate size containing the solution could be placed around it. Care was taken that the liquid always reached the same level above the thin section of the counter. The latter was carefully cleaned between successive measurements and the background redetermined. This was kept at about 23 counts per minute with the help of a heavy shield of lead blocks. A scaler and a Cenco impulse counter completed the apparatus. The activities given in Table VII are corrected for background,

TABLE VII

RESULTS OF RADIOACTIVITY MEASUREMENTS

Wet solid			Mother liquor		
Weight of sample, gm.	Weight % H_2O_2	Activity, counts/min.	Weight of sample, gm.	Weight % H_2O_2	Activity, counts/min.
76.3	7.67	6911	25.5	15.38	13747
86.4	94.79	5021	70.4	79.23	19650

dead time of counter (100 μsec.), and for decay of the radioactive material during experimentation. The calculations are as follows.

For the 7% solution the ratio of activities in the two phases is 6911/13747 = 0.5027; therefore the per cent of water in the solid phase is:

$$\frac{(100 - 7.67) - 0.5027\ (100 - 15.38)}{(1 - 0.5027)} = 100.1\%$$

Similar calculations for the 95% solution yielded exactly the same result, thereby fully confirming the above conclusions.

Discussion

The freezing point of pure hydrogen peroxide was first reported as being −1.7°C. (10). This is still often quoted in spite of the fact that it was found later to be too low by about 0.8°C. (3). More recent determinations (19) indicated definitely that the revised value, −0.89°C., was still too low. The present result, −0.461°C., is now believed to lie within a few thousandths of a degree from the true value for the following reasons: It is the highest freezing temperature observed in a direct determination; in addition it is the only result that could be duplicated to the limit of accuracy of the measurements (0.001°) and this with two different samples.

The results of calculations at zero impurity will not be considered since at least in one instance (Run No. 32) they lead to a lower temperature than the highest one obtained directly. If the correct freezing point were around −0.43°C. as suggested by runs No. 30, 37, and 39 (Table III), then the above result, −0.461°C., would correspond to a sample containing 0.03% water. Considering the difficulty of removing the last traces of water from hydrogen peroxide this is not a large quantity. However, there is no reason why exactly

the same amount of impurity should have been present in the three runs No. 37, 38, and 39 (Table II). The present investigation provides the most accurate and reliable method of ascertaining the purity of highly concentrated hydrogen peroxide. Its only drawback is the relatively large sample (70 cc.) necessary for a determination. It is planned to improve the apparatus in that respect, particularly along the lines adopted by Herington and Handley in their recent work (8).

At the time this work was begun the formation of solid solutions in the system hydrogen peroxide – water was considered an open question. In favor was the fact that fractional crystallization is extremely inefficient for concentrating hydrogen peroxide solutions. This observation, first made by Maass and Hatcher (10), has been verified repeatedly, in particular by Giguère and Maass (6), who applied the analytical, or phase separation method, and came to the conclusion that solid solutions were formed. In addition they pointed out that the freezing points of very concentrated peroxide solutions were appreciably higher than those calculated from Raoult's law.

On the other hand, these arguments were opposed by the following ones: the lattice constant of hydrogen peroxide is the same in frozen solutions (82 and 90%) as in the pure compound according to an X-ray investigation (16). More recently it has been observed in this laboratory that hydrogen peroxide solutions on cooling do not always solidify *completely* at temperatures below their corresponding eutectic, a result not easily reconciled with occurrence of solid solutions in the system (5). It is now obvious why these solutions can be supercooled with respect to the addition compound, $H_2O_2.2H_2O$; the limited stability of this hydrate is confirmed both by its low symmetry (16) and the flatness of its freezing point curve (Fig. 2).

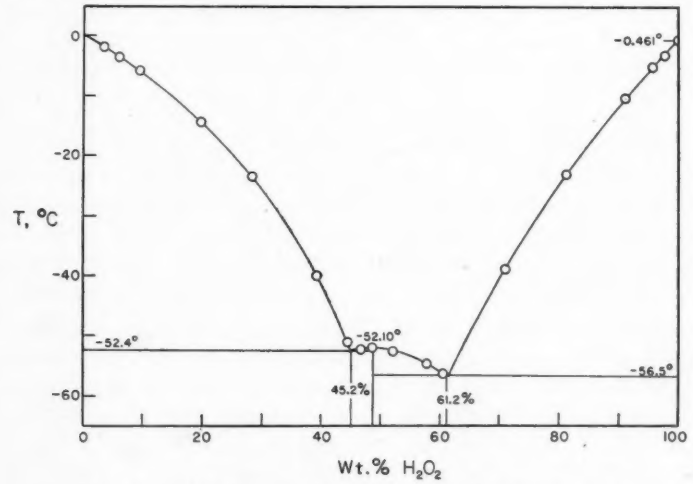

FIG. 2. *Phase diagram of the system hydrogen peroxide – water.*

From the present study and a similar one made on the system hydrazine–water (14) it must be concluded that the poor results obtained in attempting to freeze out the ice or the pure compound are due entirely to the difficulty of removing the mother liquor from the crystals. Calculations show that in most instances the solid still contained as much as its own weight of liquid although it looked quite dry. The so-called synthetic or 'wet residue' method is certainly superior to the analytical one for such investigations. In particular the use of radioactive tracers as described above should make it still more valuable and more widely applicable in the study of phase equilibria.

Finally there remained the question of deviation from Raoult's law; since dilute peroxide solutions show almost ideal behavior up to concentrations of 10% H_2O_2 it became questionable whether the accepted value, 74 cal. per gm., for the heat of fusion of hydrogen peroxide was not appreciably in error. A check of that datum by means of an ice calorimeter has yielded a value, 85.75 cal. per gm. which leads to very good agreement of the freezing point curve with Raoult's law. A description of this and other thermal measurements will be published shortly.

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Résumé

Par de nombreuses cristallisations fractionnées d'une solution à 99.6% obtenue par distillation on a préparé du peroxyde d'hydrogène d'un très haut degré de pureté. La marche des opérations était suivie en mesurant le point de congélation avec un appareil de précision et un thermomètre à résistance de platine. Le produit le plus pur ainsi obtenu se solidifiait à −0.461°C. Le point de congélation d'une vingtaine de solutions de concentrations diverses a été déterminé de la même façon. D'après le diagramme des phases du système eau-peroxyde d'hydrogène les deux eutectiques se trouvent à −52.5°, 45.2% de peroxyde et −56.3°, 60.2% respectivement. Contrairement à ce qui a déjà été rapporté l'eau et le peroxyde d'hydrogène ne forment pas de solutions solides. La preuve en a été établie définitivement par application d'isotope radioactif à la méthode dite "des résidus" de Schreinemakers.

THE EFFECT OF RELATIVE HUMIDITY ON COAGULATION AND SURFACE LOSSES OF AMMONIUM CHLORIDE SMOKE[1]

By T. Gillespie and G. O. Langstroth

Abstract

Studies have been made of the change with time in the particulate number and rate of loss to surfaces of ammonium chloride smoke at various relative humidities ranging from 15% to 98%. The results are adequately described by the theory given previously with appropriate values for the loss and coagulation constants. The rate of disappearance of the smoke increased with increasing relative humidity, particularly above a value of about 60%. This circumstance is due to an increased loss rate from the system and not to increased coagulation. Though the possibility of 'protecting' an aerosol against coagulation is remote, it would appear possible to render certain aerosols more persistent in humid atmospheres by treatment affecting loss processes rather than coagulation.

Previous studies (1, 2, 6) of the rate of disappearance of aerosols at various humidities have permitted no distinction to be made between the effect of water vapor on the coagulation process and on the mechanism of loss to surfaces. It is possible, however, to determine these separate effects by analysis of appropriate particle number and surface loss data. A suitable analytic procedure and experimental confirmation of it have been described in detail (3, 4) in connection with studies of the aging of ammonium chloride smoke under normal laboratory humidity conditions (at Ralston, 15% to 30% R.H.). This article describes studies with ammonium chloride smoke at various relative humidities ranging from 15% to 98%, leading to a description of the effect of water vapor on the coagulation and surface loss processes.

1. Apparatus and Procedure

Experiments were performed in a 0.6 m. cube chamber in 'still' air. The smoke was produced by heating 108 mgm. of ammonium chloride in an external generator as described previously (3, 4). In general, particle number and surface loss measurements were made periodically for about 100 min., but in two experiments the former were continued for more than four hours. Particle number was determined from assessment of deposits on thermal precipitator slides in the usual manner. The number of particles lost to surfaces during successive intervals in the life of the smoke was calculated from counts on replaceable slides attached to the top, bottom, and each wall of the chamber. Estimates of the apparent particle size distribution of selected thermal precipitator samples were made with the aid of a Patterson–Cawood graticule in some experiments. The details of all sampling and assessment techniques have been described elsewhere (3, 4).

[1] *Manuscript received August 21, 1950.*
Contribution from the Defence Research Board, Experimental Station, Ralston, Alberta, Canada.

To maintain the desired relative humidity in the smoke chamber, all surfaces were covered with asbestos paper soaked in water, or in a saturated aqueous solution of an appropriate salt (5). To minimize changes caused by the influx of air during smoke production, the air entering the generator was bubbled through water or the same solution. The relative humidity in the chamber was measured immediately before and after each experiment by means of an attached Assmann wet and dry bulb hygrometer; the difference between these two values never exceeded 4%. In the absence of smoke, the determined relative humidity in the chamber varied by less than 2% over a 24 hr. period both for conditions designed to produce high and low humidity.

2. Experimental Data

Particulate volume data for eight experiments are given in Table I. Surface loss data for seven experiments are given in Table II. The quantity $(\Delta n)_l$ represents the total number of particles lost to the surfaces of the chamber from the beginning of the experiment up to the time in question, divided by the volume of the chamber. It was obtained by adding together the determined losses to each surface for each successive period up to the time stated. The procedure has been described previously (3). Values of the tabulated quantities as calculated by the methods of Section 3 have been included in Tables I and II for comparison with observed results. Typical apparent particle size distributions at early and late stages in the life of a smoke are given in Fig. 1 for relative humidities of 46% and 96%.

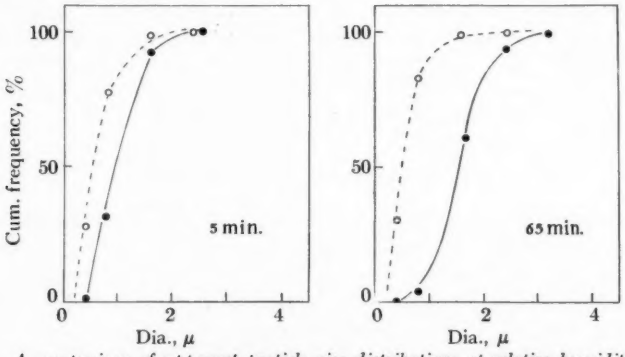

FIG. 1. *A comparison of apparent particle size distributions at relative humidities of 46% (solid lines, Expt. 15) and 96% (dashed lines, Expt. 8). The ordinates represent the percentage of particles with an apparent diameter less than the corresponding abscissa value.*

3. Analysis of the Data

It has been shown previously (3, 4) that experimental data obtained at relative humidities of 15% to 30% are adequately described by equations based on quite general grounds, i.e.,

$$\ln(1/n + k/\beta) = \beta t + \ln(1/n_0 + k/\beta) \tag{1}$$

$$\ln(n) + \beta t = -k/\beta(\Delta n)_l + \ln n_0 \tag{2}$$

$$(\Delta n)_l = \beta \int_0^t n \, dt. \tag{3}$$

TABLE I

PARTICULATE VOLUME VS. TIME DATA

Tabulated values are $10^6/n$*

Exp. #	7		8		10		11		12		14		15		17	
Relative humidity	96%		96%		96%		82%		78%		53%		46%		15%	
Time (min.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	0.95	0.85	1.12	1.06	0.7	0.7	0.6	0.6	0.76	0.74	0.73	0.8	0.78	0.9	1.10	1.10
15	1.10	1.23	1.28	1.4	1.14	1.14	0.89	1.0	0.94	1.0	1.18	1.2	1.6	1.5	1.85	1.60
25	1.7	1.6	1.8	1.9	2.0	1.6	1.2	1.3	1.18	1.3	1.8	1.5	2.5	1.9	2.2	2.1
35	2.1	2.1	2.5	2.4	1.9	2.2	1.4	1.6	1.6	1.6	1.8	1.9	2.5	2.5	2.9	2.6
45	2.0	2.6	2.2	2.9	2.2	2.8	1.7	1.9	1.8	2.0	2.3	2.3	2.1	2.8	2.6	3.1
55	2.9	3.3	3.5	3.6	3.7	3.5	2.4	2.3	2.4	2.3	2.6	2.6	3.2	3.4	3.1	3.6
65	4.1	4.0	4.1	4.3	4.1	4.3	2.4	2.6	2.3	2.7	4.1	3.1	3.9	3.9	3.1	4.1
75	4.7	4.8	5.2	5.2	5.4	5.1	2.9	2.9	3.3	3.1	4.2	3.4	3.2	4.5	5.3	4.7
85	5.1	5.7	7.6	6.1	6.1	6.1	3.8	3.3	3.8	3.5	4.1	4.1	5.4	5.1	4.8	5.2
95	8.1	6.8	8.0	7.2	7.8	7.5	5.0	3.8	4.5	3.9	3.7	4.3	5.4	5.6	5.0	5.7

* *Values under the heading 'Calc.' were obtained from Equation (1) using the constants given in Table III.*

TABLE II

SURFACE LOSS DATA

Tabulated values are $(\Delta n)_l \times 10^{-4}$ cc.$^{-1}$ *

Exp. #	8		10		11		12		14		15		17	
Relative humidity	96%		96%		82%		78%		53%		46%		15%	
Time (min.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	6.1	5.2	7.0	5.5	2.5	2.2	2.8	2.8	1.3	0.9	1.5	1.4	0.9	0.95
10	10.5	8.6	13.4	12.0	4.5	6.0	5.4	4.9	2.2	2.2	2.9	3.3	1.7	2.2
20	21.2	16.6	22.7	22.4	8.0	9.6	10.0	10.8	3.8	3.6	5.0	5.5	2.8	3.1
30	28.3	27.0	28.5	27.6	11.4	14.4	14.3	15.0	5.2	4.9	6.7	7.0	3.8	4.0
40	34.5	25.6	33.3	32.0	14.2	16.6	17.9	18.2	6.3	6.2	8.0	8.5	4.5	4.5
50	39.3	35.4	36.6	35.6	17.0	17.2	21.1	20.4	7.5	6.9	9.1	9.7	5.0	5.1
60	42.7	38.8	39.2	40.0	19.4	18.9	23.7	22.6	8.4	7.5	10.1	10.5	5.3	5.4
70	43.4	42.4	41.0	41.4	21.1	19.7	25.8	25.4	9.6	8.6	11.0	11.0	5.7	5.9
80	43.6	45.2	—	46.6	22.9	20.6	27.5	26.6	10.4	9.2	11.8	11.8	6.0	6.3
90	—	—	—	—	23.9	21.4	29.0	27.1	11.3	9.5	12.7	12.3	6.3	6.6

** The values under the heading 'Calc.' were obtained using Equation (2) and the constants as given in Table III.*

The definition of $(\Delta n)_t$ has been given in Section 2; n and n_0 denote respectively the number of airborne particles per cubic centimeter at t and at $t = 0$. The coagulation and loss constants are represented by k and β, and are defined by "coagulation rate per cc. = kn^2" and "average loss rate per cc. = βn".

Analysis of new data obtained under conditions differing from those previously studied entails (*a*) demonstration that the equations provide an adequate description of the results, and (*b*) determination of the coagulation and loss constants. Certain detailed tests of the adequacy of the theory have been described (3); a comparison of observed values of n and $(\Delta n)_t$ with those calculated using determined k, β, and n_0 values constitutes an "over-all" test. Such a comparison is made in Tables I and II. As in reference (3), the value of β was determined from the slope of the $(\Delta n)_t$ vs. $\int_0^t n\,dt$ curve, and that of k from the slope of the $\ln(n) + \beta t$ vs. $(\Delta n)_t$ plot. In a few experiments for which $(\Delta n)_t$ data were lacking, k and β were found from particle number data as in reference (4) (cf. Equation 1). The values found for the various constants are summarized in Table III, and a plot of β vs. relative humidity is given in Fig. 2.

TABLE III

A SUMMARY OF THE DETERMINED VALUES OF THE CONSTANTS IN EQUATIONS (1) TO (3)

Exp. #	Relative humidity, %	$n_0 \times 10^{-6}$	$\beta \times 10^3$ min.$^{-1}$	$k \times 10^8$ cc./min.	$k/\beta \times 10^6$
17	15	1.24	1.77	4.7	6.8
15	46	1.25	2.9	4.3	14.8
14	53	1.43	1.9	3.3	17.2
12	78	1.66	5.2	2.4	4.7
11	82	2.0	3.5	2.5	7.3
10	96	2.0	10.0	3.4	3.4
8	96	1.1	12.8	2.2	1.8
7	96	1.4	13.0	2.2	1.7
6	98	1.5	12.4	2.5	2.0
5	96	1.8	14.0	2.7	1.9

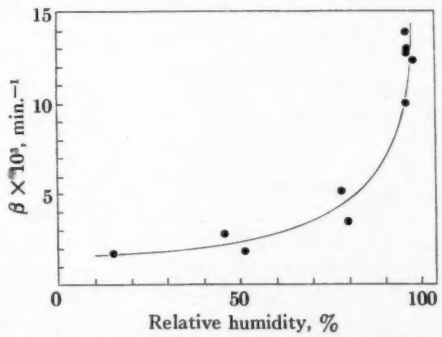

FIG. 2. *The effect of variations in relative humidity on the loss constant β.*

4. Discussion

The results show that the rate of disappearance of ammonium chloride smoke depended on the relative humidity of the atmosphere in which the particles were dispersed. For example, the number of particles remaining after 1.5 hr. at a relative humidity near 50% was about twice as great as that at a relative humidity of 96% (Table I); the number of particles lost to surfaces in this time was only about 1/4 as great (Table II). These differences are attributed to changes in the characteristics of the particles caused by sorption of water vapor.

A comparison of the calculated and observed values for particulate number and cumulative surface loss shows the agreement to be satisfactory in view of the uncertainties inherent in aerosol assessments (Tables I and II), and plots of $\int_0^t n\,dt$ and $\ln(n) + \beta t$ against $(\Delta n)_t$ were found to be linear in accordance with Equations (3) and (2). It follows that k and β remained essentially constant during an experiment as assumed in the theory, regardless of whether the relative humidity was low or high. This indicates in turn that the particles quickly reached an approximately stationary condition with respect to sorbed water vapor, since a gradual sorption would be expected to cause a gradual but marked change in β at least (cf. Fig. 2 and the remarks below). In support of this view, unpublished studies of the rate of increase in the mass of ammonium chloride smoke particles exposed to a humid atmosphere on the pan of a microbalance indicate that the sorption process is practically complete in less than 10 min.

As may be seen from Fig. 2, the loss constant β was not greatly affected by changes in relative humidity below about 60%, but thereafter increased strongly with increasing relative humidity and became nearly five times as great at 96%. This marked effect is caused presumably by an increased sedimentation rate resulting from the increased apparent density of particles on sorption of water vapor. The smokes at high relative humidity were characterized by a smaller particle size than those at low humidity, and the difference was more apparent with older smokes (Fig. 1). It could be accounted for in part by a more rapid sedimentation of the larger particles in the presence of considerable water vapor. It is interesting to note also from Fig. 1 that the median apparent particle diameter increased from about 1.1 to about 1.6μ in one hour at a relative humidity of 46%, but remained nearly constant ($\sim 0.6\mu$) at a relative humidity of 96%.

In contrast to the changes caused in β, the effect of variations of relative humidity on the coagulation constant k were not marked (Table III). There appears to be some trend, however, toward a smaller value at the high humidities. For example, the average value at 96% R.H. was 2.6×10^{-8} cc. per min. compared to 3.8×10^{-8} cc. per min. near 50% R.H. No attempt to account for this is justified at the moment in view of our lack of knowledge of the parts played by the various coagulation mechanisms.

To sum up, the rate of disappearance of ammonium chloride smoke increases with increasing relative humidity, though not strongly at values below about 60%. This circumstance is due to an increased rate of loss from the system, while the effect on the coagulation constant (if any) favors less rapid coagulation. The possibility of partially 'protecting' an aerosol against coagulation by introduction of some vapor therefore seems most remote (cf. reference (1)), but it should be possible to increase appreciably the persistence of hygroscopic aerosols in a humid atmosphere by some treatment that renders the particles incapable of sorbing moisture. Such a possibility depends on affecting loss processes other than coagulation.

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THE ALCOHOL–GLYCEROL METHOD FOR THE DETERMINATION OF FREE LIME[1]

By E. G. Swenson[2] and T. Thorvaldson

Abstract

A study was made of the alcohol–glycerol method of determining free lime in Portland cement and in mixtures of some aluminates and silicates of calcium.

Strontium chloride is an effective accelerator. Calcium chloride is effective for mixtures of the pure silicates, but with Portland cement both it and calcium acetate give reduction of the total time required only at low concentrations and produce low values for free lime at higher concentrations of the salts. Lithium chloride produces acceleration, but magnesium chloride masks the presence of free lime. Addition of water in small amounts reduces the time required for the determination; larger amounts cause high values for free lime in the presence of tricalcium silicate.

Lime heated to high temperatures becomes too inert to be determined without reactivation by suitable accelerators.

The presence of 5:3 calcium aluminate and alumina interfere with the determination of free lime. The method is not satisfactory for underburnt lime–alumina–silica systems low in tricalcium silicate but is more suitable for such systems high in this compound. The higher values obtained with accelerators are probably more accurate than those obtained without accelerators. High precision may be attained with mixtures of dicalcium silicate, tricalcium silicate, and tricalcium aluminate.

The alcohol–glycerol method (4, 8) or this method in modified form, (1, 3, 5) is probably the one most generally used for the determination of free lime in Portland cement. Extensive co-operative work (5, 6) in the evaluation of these and other methods has indicated preference for the method of Lerch and Bogue (8) on the basis of precision. The length of time required is a disadvantage, but this may be at least partly remedied by the use of barium chloride (1, 3) or sodium chloride (5) as accelerators. The wide variation in the results obtained by cement chemists in different laboratories (5), however, indicates that there are still difficulties in the execution of all these methods.

The object of the present work was to study the effect of varying conditions, the use of accelerators, and the use of the method in determining free lime in mixtures of the aluminates and silicates of calcium.

The Method

The experimental details were essentially those described by Lerch and Bogue (8). The refluxing apparatus consisted of an electrically heated double-walled asbestos board box, accommodating six 125-ml. florence flasks. Slotted

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Contribution from the Department of Chemistry, University of Saskatchewan. This paper constitutes part of a thesis submitted by one of us (E.G.S.) to the Faculty of Graduate Studies, University of Saskatchewan, in partial fulfillment of the requirements for the degree of M.A., together with additional work carried out while Assistant Professor of Chemistry at Regina College (U. of S.), Regina, Sask.

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asbestos covers fitted the necks of the flasks which were attached to 50 cm. condensers, set at an angle of 45°, the upper ends being protected by soda-lime tubes. The heating was regulated so as to keep the alcohol–glycerol solution boiling gently, and small unglazed porcelain chips were added from time to time to prevent bumping. Both corks and chips were boiled in alcohol–glycerol solution, washed and dried before use.

Unless otherwise stated, 20-min. refluxing periods were used and the final end point taken when one hour of refluxing produced no pink color in the hot solution.

Both the ethanol and the glycerol used had a water content of less than 0.3% unless otherwise stated. The latter was prepared by vacuum distillation of reagent glycerol, the middle fraction being used. Reagent grade ammonium acetate was used without being first dried, as it was found that the salt became quite acidic on drying. With reasonable protection of the ammonium acetate against absorption of moisture from the atmosphere, the amount of water thus introduced in an ordinary determination is negligible. The accelerators were anhydrous salts.

The Standardization of the Ammonium Acetate Solution

Pure reprecipitated calcium carbonate was ignited to constant weight in a platinum capsule at about 950°C., the oxide cooled in a desiccator over lime, transferred along with the emptied capsule to the dry reaction flask, shaken immediately with 60 ml. of the alcohol–glycerol (5 to 1 by volume) to prevent caking, and the solution refluxed with titrations at 20-min. intervals. Table I indicates typical results obtained with two acetate solutions, without the addition of accelerators, and with the addition of the chlorides of barium, strontium, and calcium.* In Series A, the salts were added in equal weights, while in Series B equivalent molecular proportions were used.

TABLE I

THE EFFECT OF ACCELERATORS ON THE STANDARDIZATION OF AMMONIUM ACETATE SOLUTIONS

Series	Accelerator, gm.	CaO, gm.	Initial titer, ml.	Total titer, ml.	Total time, hr.: min.	Normality obtained
A	None	0.1067	2.0	19.03	4:20	0.200
	$BaCl_2$–0.10	0.1119	6.2	20.29	3:40	0.197
	$SrCl_2$–0.10	0.1009	9.4	18.46	3:00	0.195
	$CaCl_2$–0.10	0.1013	12.3	18.29	3:20	0.197
B	None	0.1010	2.3	16.80	4:20	0.214
	$BaCl_2$–0.375	0.1007	11.4	17.12	3:00	0.210
	$SrCl_2$–0.285	0.1003	13.1	16.89	3:00	0.212
	$CaCl_2$–0.200	0.1016	13.5	16.91	4:20	0.214

* *The accelerating action of calcium chloride was observed by Mr. D. J. Trevoy in this laboratory and recorded in his Graduation Thesis, 1944.*

The accelerating effect of the salts is evident both in the increased titers at the end of the first 20-min. period of boiling and in the shorter time required to reach the final end point. While calcium chloride is very effective in increasing the first titer, it does not reduce the total time required at high concentrations. The total time is, however, subject to variations due to uncontrollable factors affecting interaction of solids and liquids.

There is a slight tendency towards lower values for the calculated normalities of the acetate solutions when the salts are used as accelerators. The differences between the normalities obtained on averaging all the experimental data available were: for calcium chloride, about 1% lower, and for barium and strontium chlorides 1½% lower than the normalities obtained in the absence of an accelerator. In the calculations of the percentage of free lime given in this paper these corrections are made where applicable.

The determinations with calcium chloride gave the poorest end points, perhaps owing to the formation of a heavy white precipitate in alcohol–glycerol solution in the presence of this salt. Strontium chloride appeared to have a slight advantage over barium chloride in the definiteness of the end point.

It was found that magnesium chloride, instead of acting as an accelerator, inhibited the process. With increasing amounts of this salt, up to a molar ratio of approximately 1½ for magnesium chloride to calcium oxide, the amount of titratable lime decreased to zero.

Increase in the length of the initial refluxing period increases the total time required and appears to increase slightly the value for the normality obtained. In a series with 0.375 gm. barium chloride present (0.1 gm. samples of CaO), and initial refluxing periods of 20, 40, and 60 min., the normality values obtained were 0.2114, 0.2123, and 0.2135, respectively. These variations, while possibly significant, are, however, of the order sometimes obtained in standardizations done at different times.

The effect of varying the weight of lime in a given volume of alcohol–glycerol solution is shown in Table II.

TABLE II

THE EFFECT OF VARYING THE WEIGHT OF LIME IN THE STANDARDIZATION OF AN AMMONIUM ACETATE SOLUTION

(0.142 gm. strontium chloride present in each instance)

CaO, gm.	Total ml. NH_4OAc solution used			Total titer, ml.	Total time, hr.: min.	Normality obtained
	1st titer	2nd titer	3rd titer			
0.0354	3.2	4.2	4.8	5.80	2:00	0.218
0.0709	5.8	7.9	10.0	11.76	2:00	0.215
0.1045	8.1	11.6	14.8	17.42	3:40	0.214
0.1380	7.5	11.5	15.8	23.00	3:40	0.214

It was also found that the addition of slightly less than the total calculated required volume of ammonium acetate solution on the first titer had no appreciable effect on the normality value obtained or on the total time. Addition of small amounts of water accelerated the process without affecting the value materially.

It is evident that considerable latitude in conditions during the standardization may be allowed without reducing the precision usually attained in the determination of free lime.

Determination of Free Lime in a Portland Cement and a Portland Cement Clinker

The alcohol–glycerol method (8) has been used in this laboratory for many years for determining free lime in Portland cement and in preparations of silicates and aluminates of calcium. In the present study no extended work with commercial cements was undertaken. For comparison, two cements were used, one a dark-colored commercial Portland cement (containing 4% ferric oxide) which had been stored in closed containers in the laboratory for 12 years, and a light-colored commercial Portland cement clinker obtained freshly burnt and unground from a cement plant.

The aged cement gave a loss on ignition of 2.33%. When this cement was received from the mill, the loss had been 0.96% and the value for free lime 1.47%. The new values for free lime were: on the unignited cement, 1.03%, thus showing a drop of almost one-third during storage, and on the cement ignited at 950°C., 2.01%. All the determinations were made without accelerators. It would thus appear that approximately one third of the original free lime had been fixed by carbon dioxide during storage, this reappearing on ignition, while an additional one half of one per cent of free lime was liberated on ignition, probably through decomposition of superficially hydrated tricalcium aluminate (9) and tricalcium silicate (7). Practically all the increase in free lime on ignition appeared as increases in the first two 20-min. titers. The time of determination for the ignited and unignited samples was practically the same: without accelerators seven to eight hours, with accelerators two to three hours. In six individual determinations done at random over a period of two years on the ignited cement, using no accelerator, the maximum free lime obtained was 2.18%, the minimum 1.87%, the mean 2.01%, and average deviation from the mean, 0.09%. Carefully conducted series of determinations gave greater precision.

In agreement with published reports (1, 3, 5) it was found that the addition of barium chloride reduced the time per determination to less than one half, but gave free lime values somewhat higher than those obtained with no accelerator present. Strontium and lithium chlorides were found to have much the same effect. Calcium chloride gave acceleration when used in low concentrations, but the free lime values were low when more than 0.5 gm. of the salt was

present with no decrease, or even an increase, in the time required. A heavy flocculent precipitate obscures the end point. The addition of small amounts of calcium acetate,* a product of the titration, produced acceleration, but larger quantities gave a gelatinous precipitate and low values for free lime, suggesting a possible weakness in the method when free lime is present in some quantity. The addition of 0.3 gm. of magnesium chloride per determination, or an equivalent amount of magnesium acetate, completely masked the presence of free lime.

The introduction of water in small quantities to the reaction mixture reduced the total time and caused no appreciable increase in free lime values. On addition of more than 0.5 ml. of water per 60 ml. of alcohol–glycerol solution the free lime values obtained increased gradually with increase in the total time, apparently owing to the progressive hydrolysis of cement compounds.

The freshly burnt cement clinker which was ground to pass 200 mesh and which gave an ignition loss of 0.19% was found to have a free lime content of 0.40%. The values for the ignited and unignited samples agreed within experimental error. With various amounts of the chlorides of barium, strontium and calcium as accelerators, and with water, the results obtained were analogous to those for the cement.

Determination of Free Lime in Mixtures of Tricalcium and Dicalcium Silicates

These two silicates constitute about 75% of normal Portland cement clinkers. The sample used was an underburnt mixture of lime and silica of high purity containing only the two silicates and calcium oxide. The average of eight determinations without an accelerator gave 1.72% free lime. The average time was about $4\frac{1}{2}$ hr. and the end points were very definite.

The chlorides of barium and strontium showed about the same accelerating effect as with Portland cement. Calcium chloride was just as effective as, or more effective than, the other salts; thus its behavior with the silicates differed from its behavior with Portland cement, but the flocculent precipitate produced made the determination of the end point more difficult. Strontium chloride gave the best end points. Addition of magnesium chloride masked the presence of free lime. The free lime values were slightly higher with barium and strontium chlorides than with no accelerator. The bromide and nitrate of strontium are also effective accelerators. Table III shows the effect of strontium chloride on the process.

The substitution of "reagent" glycerol, containing 4.4% water, for the distilled glycerol (less than 0.3% H_2O) shortened the time to about the same extent as using 0.5 to 1.0 gm. of the chlorides and gave a normal free lime value of 1.73%.

* *The accelerating action of calcium acetate was observed by Herbert Johnson in this laboratory. Can. J. Res. B, 21: 236. 1943.*

TABLE III

EFFECT OF STRONTIUM CHLORIDE ON THE DETERMINATION OF FREE LIME IN A SAMPLE OF CALCIUM SILICATES

$SrCl_2$, gm.	Sample weight, gm.	Initial titer, ml.	Total titer, ml.	Total time, hr.: min.	% Free lime obtained
None	1.0094	0.1	2.96	6:00	1.73
0.50	1.0033	1.6	3.00	3:20	1.74
1.00	1.0026	2.0	3.03	4:00	1.76
1.50	0.9957	2.2	3.14	1:40	1.84
2.00	1.0030	2.3	3.11	2:20	1.81

The addition of water produced similar results with this sample as with the cement and the cement clinker, indicating that the increase in the free lime values above a limiting quantity of water is due to the hydrolysis of the silicates in the cement.

The use of excess of the ammonium acetate solution at the first titration had no apparent effect on the values obtained for free lime or any marked effect on the total time, nor was there any significant difference when the sample was ground to pass a 100 or a 200 mesh sieve. The determination of free lime in a mixture formed by the addition of calcium oxide to the above sample of silicates gave the expected calculated value.

In general, the determination of free lime in this type of solid material was found to be considerably easier than in the cement and cement clinker. End points were more definite than with commercial cements and the precision was much greater.

Determination of Free Lime in Solid Systems containing Calcium Aluminates

In a properly fired Portland cement the alumina is probably present partly as tricalcium aluminate and partly as a calcium aluminoferrite. At temperatures above the incongruent melting point of tricalcium aluminate the 5:3 aluminate is probably produced. The 5:3 aluminate may also be present in "underburnt" systems. The effects of the presence of these aluminates on the determination of free lime was studied using mixtures in the form of clinkers or the pure compounds prepared in the laboratory.

All ignitions were made in platinum, below 1000°C. in an electric muffle furnace and above this temperature in an induction furnace. Unless otherwise stated, each firing at the higher temperature was for a period of 45 min. to one hour. After each ignition, the product was ground to pass a 200-mesh sieve and remixed thoroughly.

Pure alumina and calcium carbonate were proportioned by weight to give, if properly combined, tricalcium aluminate and about 2% free lime. After a preliminary ignition at 950°C., Sample A was heated for one-half hour to

partial fusion at above 1535°C. for the purpose of forming some 5:3 calcium aluminate. Sample B was fired twice at about 1480°C. Sample C was part of Sample B given a third ignition at about the same temperature. After the last ignition the sample was softly sintered and probably contained only tricalcium aluminate plus free lime.

Table IV gives the data for the determination of free lime in these samples. For A, the total time was exceedingly long even with accelerators present; end points were hard to judge, and the final end points were rather uncertain. In Sample B, which had been given two ignitions below the transition point, the alumina being probably mostly in the form of tricalcium aluminate, the time was still very long but was greatly reduced with barium chloride and calcium chloride present, and the end points were much improved. Sample C, with three ignitions, also required an excessively long time when no accelerator was present, but with large amounts of strontium chloride the time was radically reduced and the end points were quite good.

TABLE IV

EFFECT OF IGNITION TREATMENT ON DETERMINATION OF FREE LIME IN LIME–ALUMINA MIXTURES

Sample and ignition temperature	Accelerator, gm.	Sample weight, gm.	Initial titer, ml.	Total titer, ml.	Total time hr.: min.	% Free lime obtained
A	None	0.5220(*a*)	0.5	8.89	61:00	10.1
> 1535°C.	None	0.5362	0.5	9.63	61:00	10.6
	$BaCl_2$–0.526	0.5261	3.9	9.61	20:00	10.7
	$SrCl_2$–0.511	0.5113	4.9	9.52	20:00	10.9
B	None	0.5026	0.1	2.15	24:30	2.53
1480°C.	None	0.5264	0.0	2.01	24:30	2.26
(twice)	$BaCl_2$–0.501	0.5007	1.3	2.15	3:00	2.50
	$CaCl_2$–0.506	0.5064	2.0	2.07	1:40	2.40
C	None	0.9945	0.0	2.52	22:20	1.50
1480°C.	$SrCl_2$–0.100	1.0019	0.6	2.51	22:20	1.46
(thrice)	" –0.500	0.9974	1.3	2.86	5:00	1.67
	" –1.000	1.0014	1.7	2.83	2:30	1.65
	" –1.000	1.0055(*b*)	2.2	2.90	1:40	1.68

(*a*) *100-mesh.* (*b*) *Re-ignited at 950°C.*

Several possible explanations may be proposed for the extremely long time required for the determinations reported in Table IV and for the differences in the behavior at the end points:

(*a*) The physical condition of the material brought about by partial fusion.

(*b*) The formation of "hard-burnt" unreactive calcium oxide at the high temperature.

(*c*) That the presence of the 5:3 aluminate by some unknown mechanism lengthens the time required and obscures the end point.

As to (*a*), it was found that the fineness of the sample had only a minor effect on the time required and on the value for free lime obtained. Thus the sample

in the first determination of Table IV was ground to pass a 100-mesh sieve, the second and all other samples were ground to pass a 200-mesh sieve.

As to (*b*), inactivation of calcium oxide at high temperatures has been reported by several experimenters (2). To test this further a sample of lime was ignited at about 1535°C. and its behavior compared with a sample ignited at 950°C. Table V gives the results of the comparison.

TABLE V

THE EFFECT OF IGNITION AT HIGH TEMPERATURES ON THE TITRATABILITY OF LIME IN ALCOHOL–GLYCEROL SOLUTION
(0.1 gm. samples of lime)

Ignition treatment	Accelerator, gm.	Total time, hr.: min.	Normality obtained for acetate solution
Ignition at 950°C. for 17 hr.	$SrCl_2$–1.0	1:00	0.205
	None	4:20	0.205
Ignition at 1535°C. for 20 min.	$SrCl_2$–1.0	1:00	0.204
	None	40% lime titrated after 5½ hr. of boiling.	

It is evident that at high temperatures calcium oxide becomes very unreactive to the alcohol–glycerol mixture but is readily reactivated by the presence of strontium chloride, thus behaving like samples B and C of Table IV. Other experiments indicated that this inactivation of calcium oxide is noticeable at a temperature of 1150°C.

The behavior of Sample A of Table IV only partly fits this pattern. It seemed possible that the presence of the 5:3 calcium aluminate has an adverse effect both on the time required and the definiteness of the end point. This question was further investigated.

In preliminary experiments, a sample of tricalcium aluminate which was deficient in lime and therefore contained some 5:3 aluminate was used. One-gram samples of this were mixed with 0.1 gm. of pure ignited calcium oxide and the usual determination of free lime made on the mixture. With no accelerator the determination was only 64% completed in 11 hr. as against a normal total time for completion for lime alone of about four hours under the same conditions. The end points were also more difficult to judge. With barium chloride or strontium chloride, the time was reduced but was longer than normal. After three ignitions with excess of lime at 1450°C. to transform all the 5:3 aluminate into tricalcium aluminate, the determination of free lime, using 1 gm. of strontium chloride, became normal both as to the time required and the definiteness of the end point.

Three series of experiments were carried out with mixtures of calcium oxide and 5:3 calcium aluminate, the latter ground to pass a 200-mesh sieve. In Series A (Table VI, Expts. 1, 2, 3, and 4) the amount of the 5:3 compound

was varied, the amount of calcium oxide (ignited separately at 950°C.) being almost constant. During the first two 20-min. periods of refluxing, no accelerator was present. This showed that the initial titer obtained decreased with the increase in the 5: 3 compound present. Then 1 gm. of barium chloride was added and the determination carried to an end point. There was a marked increase in total time owing to the presence of the aluminate and also all the lime added was not accounted for, the deficiency increasing with the amount of aluminate. End points were difficult to judge in all the runs in which this aluminate was present. At the end point accepted, the solid had a red coloration thus suggesting incompleteness while the supernatant liquid remained colorless for one hour of refluxing.

The data of Series A (Table VI) suggest that under the conditions of the determination, the 5: 3 aluminate may combine with or in some way neutralize calcium oxide. Series B (Expts. 5, 6, 7, 8, and 9) was designed to determine whether such disappearance of free lime is increased by increasing the length of the refluxing period before titration, or by using no accelerator, or by delaying its addition. It is evident that using no accelerator (No. 7 vs. No. 6) accentuates the disappearance of free lime; that using long refluxing periods at the start and delaying the addition of the catalyst (Nos. 8 and 9 vs. nos. 5 and 6) both increases the total time and the disappearance of free lime. The statements re the end points in Series A apply here also. Another sample of 5: 3 calcium aluminate used in Series C (Expts. 10, 11, 12, 13, and 14) was freshly ignited, a very long initial refluxing period was used, and the amount of lime added increased by steps. This also shows the progressive disappearance of free lime, increasing with the amount of free lime present. In this series, the solid remaining at the end point was not colored, and the end points were easier to determine than in Series A and B.

The presence of the 5: 3 calcium aluminate appears to reduce the initial titer, lengthen the total time required, and give lower values for free lime. The length of time which the solution is in contact with the lime and aluminate accentuates, and the presence of accelerators reduces, these effects.

The above observation on the effect of the 5: 3 calcium aluminate on the determination of free lime is of interest in connection with the work of Thorvaldson and Schneider (10) on the thermal decomposition of the hexahydrate of tricalcium aluminate and the composition of the aluminate formed. One might suspect that here is the explanation of the low values for free lime obtained by these workers, leading them to favor the formula, $12CaO.7Al_2O_3$, in place of $5CaO.3Al_2O_3$, for the aluminate produced by the thermal decomposition. However, under the conditions they used the determination of free lime in the thermal decomposition product of the hexahydrate was very rapid (most of the free lime being titrated with three five-minute periods of boiling), and the determination had none of the adverse characteristics observed with the mechanical mixture of calcium oxide and 5: 3 calcium aluminate prepared by ordinary thermal methods. Thus, the aluminate formed on thermal decom-

position of the hexahydrate of tricalcium aluminate (10) at temperatures between 550° and 950°C. does not have the same properties as the product formed by the thermal interaction of lime and alumina in the molar ratio 5: 3 at higher temperatures (Table VI).

TABLE VI

THE EFFECT OF 5: 3 CALCIUM ALUMINATE (C_5A_3) ON THE DETERMINATION OF FREE LIME

Expt. No.	Initial reflux period before 1st titer, hr.: min.	Added C_5A_3, gm.	CaO, gm.	Initial titer, ml.	Total titer, ml.	Total time, hr.: min.	% of added lime determined
Series A.	*1.0 gm. barium chloride added after two 20-min. refluxing periods*						
1	0: 20	None	0.1036	2.3	17.56	3: 20	Taken as 100
2	0: 20	0.5083	0.1019	1.9	16.87	8: 00	98
3	0: 20	1.0027	0.1011	1.0	15.37	6: 00	90
4	0: 20	1.5121	0.1029	0.9	12.51	8: 00	72
Series B.	*5 and 6, 1.0 gm. $BaCl_2$ added at start; 7, no accelerator; 8, 1.0 gm. $BaCl_2$ added after 1 hr. 20 min.; 9, 1.0 gm. $BaCl_2$ added after 2 hr. 20 min.*						
5	0: 20	None	0.1029	14.2	17.39	1: 40	Taken as 100
6	0: 20	0.9360	0.1048	12.4	17.19	4: 20	97
7	0: 20	0.9996	0.1007	1.3	14.93	9: 40	89
8	1: 20	0.9344	0.1047	3.1	15.75	9: 00	89
9	2: 20	0.8999	0.1005	3.1	12.27	11: 30	72
Series C.	*1.0 gm. strontium chloride added at start*						
10	0: 20	None	0.1011	16.3	16.98	0: 40	Taken as 100
11	22: 30	0.5004	0.1948	9.2	31.32	6: 30*	95.6
12	22: 30	0.5004	0.2050	8.7	32.11	9: 30*	93.1
13	22: 30	0.5009	0.2168	8.9	33.74	10: 30*	92.5
14	22: 30	0.5002	0.2259	8.7	34.66	10: 00*	91.2

* *Not counting initial refluxing period.*

It was found that the presence of monocalcium aluminate interferes with the determination of free lime, increasing the time required, giving low values and poor end points. The use of barium chloride, however, largely counteracts these effects.

The presence of free alumina also interferes in a similar manner. Hydrated alumina is most effective in lowering the value for free lime. Full values for the lime added are obtained in the presence of alumina which has been ignited at 1300°C. but the time required is still longer than with the lime alone.

The determination of free lime in the presence of tetracalcium aluminoferrite (1 part of lime to 10 parts of compound) presented some difficulty in the observation of the end point, but all the calcium oxide was titratable.

The Determination of Free Lime in Laboratory Clinkers Containing Lime, Alumina, and Silica

In the preparation of samples, all clinkers were ground after each firing to pass a 200-mesh sieve.

The first sample studied was a clinker made in the laboratory by repeated firings until tests for free lime were negative. By calculation, after allowing for the effect of small amounts of ferric oxide and magnesium oxide, it contained 51% dicalcium silicate, 24% tricalcium silicate and 24% tricalcium aluminate. It was then fired in the induction furnace at slightly above 1535°C. for 16 min. after which 20 hr. of refluxing with the alcohol–glycerol mixture with accelerator gave a value of 0.23% for free lime. After a second such firing for eight minutes, with rapid cooling in air, the same value was obtained in 15 hr. of refluxing. Two other samples fired at about 1600°C. for 15 and 35 min. respectively, the platinum crucible being quenched in water, gave a negative test for free lime in the final product after one hour of refluxing. It appears therefore that, at these temperatures, the lime liberated by the decomposition of the tricalcium aluminate combines very rapidly with the dicalcium silicate or that the method for determining free lime fails with this material. There is also the possibility that at the time of quenching all the tricalcium aluminate had been decomposed to the 5:3 compound and that the dicalcium silicate, of which there is a large excess, had combined with all the lime liberated in the process.

Addition of 1 gm. of the original clinker to 0.05 and 0.10 gm. samples of pure calcium oxide increased materially the time of refluxing required, and the addition of the same amount of the product fired above 1600°C. increased the time required still further.

A second clinker of similar composition was then prepared from pure calcium carbonate, alumina, and silica in such a way as to leave a small amount of free lime in the product. The calculated composition for complete combination was: dicalcium silicate 52%, tricalcium silicate 24%, and tricalcium aluminate 24%. Two consecutive firings, one of 45 min. and the other of 25 min. were made in the clinkering range below 1535°C. A free lime determination on the product with 0.5 or 1 gm. of strontium chloride required over 20 hr. and gave a value of 1.2% calcium oxide. Without an accelerator the time required was more than 30 hr. and the value for free lime 0.9%. The end points were poor and the behavior of the product reminded one of the aluminates of Table IV.

Both the ternary clinkers so far used were by calculation relatively high in dicalcium silicate and low in tricalcium silicate. A third, slightly underburnt clinker high in tricalcium silicate was therefore prepared from pure materials. For complete combination the calculated composition was dicalcium silicate 7.5%, tricalcium silicate 68.5%, and tricalcium aluminate 24%. This was fired twice slightly below 1535°C., first for 45 min. with the production of a hard clinker and then for 35 min. giving a softer sintered mass. Using accelerators the time required for a free lime determination was 3½ to 4 hours and the value 2.5% calcium oxide, and without an accelerator a value of 1.9% was obtained

after 10 hr. of refluxing. The behavior of this sample did not differ greatly from that of some commercial Portland cements. The end points without an accelerator were poor but improved with the use of the chlorides of either barium or strontium.

On adding 5% magnesium oxide to this clinker and heating for 25 min. between 1450° and 1500°C. with quenching of the crucible in water, the value obtained for free lime (with barium chloride as accelerator) was increased to 5.4%. The time of refluxing required was also increased materially.

The experiments with lime–alumina–silica laboratory clinkers indicate that the alcohol–glycerol method for determining free lime is too lengthy and gives results of doubtful accuracy for underburnt clinkers low in lime, without the use of accelerators, but may give somewhat more reliable results with underburnt clinkers high in lime. It seems probable that the clinkers giving unsatisfactory results contain active aluminum compounds of lower lime content than tricalcium aluminate, possibly the 5:3 calcium aluminate. High temperatures cause the free lime to become inert and lengthen the process of extraction with the alcohol–glycerol mixture. These adverse effects may be accentuated simultaneously by conditions such as the rapid passage of a partly reacted mix from the zone of medium to that of high temperature, as was the case with the samples of Table IV and the ternary clinkers studied above. Through the reactivation of inert calcium oxide and the speeding up of the extraction process, the use of suitable accelerators probably gives more accurate values for free lime in such "difficult" clinkers. One may conclude that, whenever the time of the determination of free lime is abnormally lengthy, the results should therefore be suspect.

The experiments described were all made with a highly anhydrous alcohol–glycerol mixture, usually containing not more than 0.1% water. It is possible that the time required for a determination of free lime could be materially reduced by using a less anhydrous mixture without introducing serious error.

The Mechanism of the 5:3 Calcium Aluminate Effect

The basic chemistry of the alcohol–glycerol determination of free lime, which needs further study, will not be discussed here. Analysis of the solid formed during the digestion of calcium oxide indicated that it is a mixture of mono- and diglycerates of calcium. The presence of the 5:3 calcium aluminate produces three effects. First, the reaction which changes the calcium oxide to a titratable form appears to be retarded as shown by the progressively decreasing first titers with increasing amounts of the aluminate, and by the increase in the total time required. Successive 20-min. titers then increase gradually to a maximum, probably owing to the accelerating action of the calcium acetate and of the water formed during the titration, and then taper off. Second, the amounts of calcium oxide, as measured by titration, tend to be reduced. Third, end points become very difficult to judge. The first two effects are partly counteracted by the use of suitable accelerators.

The first effect appears to be due to dehydration of the alcohol–glycerol mixture by the aluminate. There are reasons to expect this, as reaction with water produces two substances of extremely low vapor tension, tricalcium aluminate hexahydrate and a monohydrate of alumina. The calculated maximum removal of water by this reaction is equal to about one-third of the weight of the 5:3 aluminate. The accelerating effect of water in the determination of free lime has been mentioned. If the amount of water in the mixture is decreased, the rate of production of the titratable combination of calcium oxide is progressively reduced as a completely anhydrous system is approached. It was found that the reduction in the initial titer with the 5:3 aluminate is most marked with alcohol–glycerol mixtures containing very small but appreciable amounts of water. In parallel determinations of lime with and without the addition of the 5:3 aluminate, starting with a nearly anhydrous alcohol–glycerol mixture, progressive additions of very small quantities of water rapidly increased the first titer for the pure calcium oxide, but had very little effect on the first titer for the mixture of calcium oxide and 5:3 calcium aluminate until a critical ratio for water to aluminate had been reached. This critical ratio varied with different samples of the 5:3 aluminate of practically the same chemical purity, apparently owing to differences in reactivity, produced by conditions during their preparation. Further parallel experiments refluxing pure calcium oxide (1) with an alcohol–glycerol solution which had been given a preliminary refluxing with 5:3 calcium aluminate and decanted, and (2) with the original solution, gave in the first case the 5:3 aluminate effect of the smaller initial titer and longer total time.

The second effect, the low value for free lime, is probably due to a chemical reaction of the calcium oxide with the 5:3 aluminate. When an effective accelerator is used with short intervals between titrations the error thus introduced may not be significant, but when the early titers are small and the determination is prolonged due to the absence of accelerators (including water) the error may become appreciable.

The third effect, the indefinite end point, may be due to a slow reversal of the process by which calcium oxide is removed by the 5:3 aluminate. The difficulty is not due to adsorption of the indicator as increasing its concentration does not give any improvement.

If the first effect of the 5:3 aluminate, the reduction in the initial titer and the lengthening of the time required for the determination, is due to dehydration, it is evident that any powerful dehydrating agent, which is otherwise inert as far as the process is concerned, should slow up the process without introducing error in the final result. This appears to be the case. Addition of tricalcium aluminate to calcium oxide was found to increase the time of refluxing required but the end points were good. Addition of barium chloride brought the time required back to normal. The addition of 1 gm. of a mixture of silicates containing 92% tricalcium silicate to 0.1 gm. of calcium oxide more than doubled the time necessary to titrate the free lime, but the end points

were not affected and the calculated values for free lime were obtained. The behavior of hydrated alumina on ignition, reported above, indicates that its capacity to combine rapidly with lime is destroyed by heating before it loses its capacity to remove water from the reaction mixture. When cement containing no free lime is introduced into the reaction flask containing the alcohol–glycerol mixture with pure calcium oxide, the time for the titration is greatly increased but all the free calcium oxide is recovered. One would expect the effect to vary considerably with different cements, depending mainly on their content of tricalcium aluminate and tricalcium silicate, the two chief dehydrating agents present, but also probably on the conditions of manufacture of the cement.

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EXCHANGE REACTIONS OF IODIDE ION WITH AROMATIC IODIDES[1]

By A. M. Kristjanson and C. A. Winkler

Abstract

The exchange reactions of iodide ion with *o*- and *p*-nitroiodobenzene in the temperature range about 170°–238°C. were apparently second order with activation energies of approximately 29 and 33.5 kcal. per mole respectively. In the same temperature range the exchange of iodide ion with iodobenzene and *m*-nitroiodobenzene appeared to be first order reactions, with activation energies of approximately 25 kcal. per mole.

Introduction

The use of radioactive isotopes to investigate nucleophilic substitution at an aromatic carbon atom has received only limited attention. It has been reported that bromide ion does not exchange with bromobenzene (1) and that iodide ion does not exchange with iodobenzene, *p*-nitroiodobenzene, or *p*-nitroaniline at 100°C. in ethanol, nor with *m*- and *p*-iodobenzoic acids at 100°C. in acetone (5). With diphenyl iodonium iodide at room temperature in aqueous ethanol, only the negatively ionizing iodine exchanges with iodide ion (4). Exchange of bromine has been observed between bromobenzene or 1-bromonaphthalene, and aluminum bromide, but no reaction of these aromatic bromides occurred with potassium, cupric, or antimony bromides (7). Both iodine and iodide ion have been found to exchange with *l*-diiodotyrosine in aqueous solution and with 3,5-diiodo-*p*-cresol, 2,6-diiodophenol, 4,6-diiodophenol, and 2,4,6-triiodophenol in aqueous methanol (6).

The only kinetic study of exchange between halide ion and an aromatic halide is that of Sugden and Lu (9), who determined the second order velocity constants and activation energy for the exchange between lithium bromide and 2,4-dinitrobromobenzene in ethylene glycol diacetate solution in the temperature range of 70.3° to 130.1°C.

In the present investigation the exchange reactions of sodium iodide with iodobenzene and with *o*-, *m*-, and *p*-nitroiodobenzenes have been studied kinetically by working at temperatures higher than those used in previous unsuccessful attempts to effect such exchanges.

Experimental and Results

Radioactive I^{131} was obtained as carrier-free sodium iodide from the National Research Council Atomic Energy Project, Chalk River. Merck reagent grade sodium iodide, dried at 120°C. for several days, was used as diluent for the radioactive material.

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Iodobenzene from Brickman and Co., Montreal, was fractionated to obtain an experimental sample boiling at 189.1–189.2°C. The nitroiodobenzenes were also from Brickman and Co., and had the following characteristics after recrystallization:

o–Nitroiodobenzene — m.p. 51°C., b.p. 284°C.
m–Nitroiodobenzene — m.p. 37°C., b.p. 280°C.
p–Nitroiodobenzene — m.p. 171°C., b.p. 284°C.

The rate of reaction was followed by determining the change in specific activity of a silver iodide precipitate obtained from appropriately treated solutions of the inorganic or organic iodide. The silver iodide, after being washed with hot nitric acid, was slurried in anhydrous methanol and poured into a glass collar ground to a leak-proof fit on the surface of a glass plate. After evaporation of the methanol and removal of the collar, a uniform deposit of silver iodide remained, the activity of which was determined with standard counting equipment. The weight of silver iodide taken was 20 to 60 mgm., over which range experiment showed errors from weighing and self-absorption to be less than 1%.

Reaction mixtures were contained in sealed Pyrex glass tubes. Vapor thermostats were used, the temperatures of which were determined by the boiling points of pure liquids. From time to time a tube was removed, the contents extracted with benzene, and the iodide in the aqueous layer precipitated with silver nitrate. If it was desired to determine the activity of the aromatic iodide, the benzene layer was washed with water until free of halogen and the aromatic iodide then converted to inorganic iodide by catalytic hydrogenation in alkaline solution as described by Schwenck, Papa, and Ginsberg (8). After hydrogenation, the catalyst was removed by centrifuging, and filtering, and the clear filtrate treated with nitric acid and silver nitrate.

Preliminary experiments with ethylene glycol diacetate as solvent showed exchange to occur between sodium iodide and iodobenzene at temperatures of 150–250°C., but the solvent was simultaneously attacked by sodium iodide. Ethanol and acetonitrile were found to be unaffected by sodium iodide in the same temperature range during periods of more than 200 hr. Acetonitrile was chosen as the solvent for further work owing to its lower vapor pressure at the relatively high temperatures used.

The value of the rate constant recorded for a given temperature is, with a few exceptions, the average of individual values for different reaction times with the particular concentration conditions indicated. Two or more reaction times were generally used. The mean deviation of the individual values of k from the average was usually less than $\pm$ 10%, but seldom less than $\pm$ 5%.

Exchange of Sodium Iodide with o-Nitroiodobenzene

In Table I are given the results for the exchange of sodium iodide with *o*-nitroiodobenzene, the aromatic iodide which exchanged the most rapidly of those studied, and for which the experimental results are the most extensive.

TABLE I

THE EXCHANGE OF SODIUM IODIDE WITH *o*-NITROIODOBENZENE

Temp. °C.	Reactant conc., molarity		Maximum exchange, %	$k \times 10^3$ liter-mole^{-1} hr.$^{-1}$
	NaI	o-$NO_2.C_6H_4I$		
238	0.037	0.147	87.5	596
	0.147	0.037	65.5	319
207	0.076	0.038	62	70.5*
	0.038	0.076	72	89
	0.038	0.153	50	93
	0.153	0.038	42	65
	0.076	0.153	34	88 (single value)
185	0.039	0.158	85	30
	0.158	0.039	59	13.6
	0.079	0.158	62	25.5
157	0.041	0.164	63	7.1
	0.164	0.041	24	2.3
	0.082	0.164	36	4.4
	0.082	0.328	98	12.4
	0.328	0.082	55	1.8*
122	0.086	0.171	42	1.0
100	0.088	0.176	30	0.26
	0.044	0.176	43	0.46
	0.176	0.044	6	0.05

* *Determined from increase in activity of organic iodide.*

It will be noted that the calculated constant increased as the ratio of aromatic to inorganic iodide was increased, this increase being more pronounced the lower the temperature. Empirically, log k at a given temperature varies in approximately linear manner with the square root of the ratio of aromatic iodide concentration to inorganic iodide concentration.

A plot of log k against $1/T$, for a given ratio of aromatic iodide to inorganic iodide concentrations, gives a straight line in the temperature range about 170°C. to 238°C., corresponding to an activation energy of approximately 29 kcal. per mole. At lower temperatures there is distinct curvature of the Arrhenius line in the sense of a smaller temperature dependence of the reaction rate, but the data are inadequate for a proper evaluation of the activation energy in the lower temperature range, where the rate of exchange became inconveniently slow.

Assuming reaction to be between the aromatic iodide and iodide ion derived from sodium iodide, error in calculating the rate constants is introduced into the concentration term for the inorganic iodide by ignoring the change in degree of dissociation of sodium iodide in acetonitrile with change of concentration. At the boiling point of acetonitrile (*ca.* 80°C.), sodium iodide is approximately 85% dissociated in 0.05 M solution, and about 50% dissociated

in 0.20 *M* solution (2). If it is assumed that the change in degree of dissociation with concentration is the same at the temperatures used in the present study as it is at 80°C., correction can be applied to the calculation of the velocity constants. When this is done, the discrepancy between the calculated velocity constants with different ratios of aromatic to inorganic iodides is largely eliminated for temperatures above 185°C. At lower temperatures, however, the calculated values of k still increase with increase in the ratio *o*-nitroiodobenzene: sodium iodide. Since the basis of the correction is somewhat uncertain, corrected k values are not tabulated. However, the fact that such a correction does operate in the sense of improving the second order rate constants makes it seem probable that the reaction is essentially first order with respect to both aromatic iodide and iodide ion in the region of higher temperatures. At sufficiently low temperatures the principal mechanism may be altered, possibly to one with a first order rate-controlling step.

It would appear from the results at 207°C. and 157°C. that the calculated k values increase with increase of aromatic iodide concentration at given sodium iodide concentration. This effect, which seems to be more marked at the lower temperature, is further indication, perhaps, of the occurrence of some reaction other than a second order exchange.

During the exchange of sodium iodide with *o*-nitroiodobenzene, traces of free iodine (5×10^{-7} mole) were formed after about 30% exchange. There was no indication that its presence had any influence on the velocity constant for the exchange reaction.

Exchange of Sodium Iodide with p-Nitroiodobenzene

An exception to the general method of analysis was made for *p*-nitroiodobenzene. The contents of a reaction tube was transferred to a 50 cc. centrifuge tube containing 25 cc. of cold water, and cooled to promote nearly complete crystallization of *p*-nitroiodobenzene. The mixture was centrifuged and the clear liquid decanted and analyzed for sodium iodide activity if desired. The solid *p*-nitroiodobenzene was washed with water until the wash water gave no test for halogen, and was then reduced to inorganic iodide by catalytic hydrogenation. Silver iodide was then precipitated as before for determination of activity. Experiment showed that analysis for either reactant gave concordant results.

The range of *p*-nitroiodobenzene concentrations used in the experiments was limited by its solubility in acetonitrile. The data obtained for the exchange rate at various temperatures and concentrations of inorganic and aromatic iodide are summarized in Table II. There is little doubt that the reaction at higher temperatures is of the same order in respect of both reactants. The experiment at 207°C. with 0.037 *M* sodium iodide and 0.190 *M* aromatic iodide clearly indicates that the reaction is second order over-all, hence first order with each reactant.

TABLE II

THE EXCHANGE OF SODIUM IODIDE WITH *p*-NITROIODOBENZENE

Temp. °C.	Reactant conc., molarity		Maximum exchange, %	$k \times 10^2$ liter-mole^{-1} hr.$^{-1}$
	NaI	p-$NO_2.C_6H_4I$		
238	0.037	0.074	66	178
	0.074	0.037	55	128
207	0.076	0.037*	53	17.5
	0.037	0.076*	61	19.3
	0.076	0.037	64	17.4
	0.037	0.076	64	21.7
	0.076	0.037	53	17.1
	0.037	0.190	48	18.0
185	0.039	0.079	50	4.6
	0.079	0.039	39	3.5
157	0.041	0.082	20	0.76
	0.082	0.041	13	0.52
100	0.044	0.088	12	0.16
	0.088	0.044	0.25	0.003

* *p-Nitroiodobenzene sublimed.*

At the higher temperatures, the increase in velocity constant with increased ratio of aromatic iodide to sodium iodide is largely eliminated if correction is applied for the change in degree of dissociation of sodium iodide, on the basis indicated previously for *o*-nitroiodobenzene.

The Arrhenius line for given concentrations of inorganic and aromatic iodides is straight over a temperature range of about 170° to 238°C., corresponding to an activation energy of 33.5 kcal. per mole. At lower temperatures, the line is markedly curved in the sense of smaller temperature dependence but the results at 100°C. are not sufficiently accurate to permit evaluation of the activation energy in this temperature region.

Exchange of Sodium Iodide with m-Nitroiodobenzene

The results obtained for the exchange of sodium iodide with *m*-nitroiodobenzene in acetonitrile are summarized in Table III. The values at 238°C. are subject to uncertainty from secondary reactions which produced appreciable amounts of free iodine as well as trace amounts of black precipitate.

It is evident that the first order constants (last column), calculated on the assumption that the rate depended only on the concentration of aromatic iodide, show much better agreement than the second order constants for varying concentrations of reagents. The activation energy calculated from the first order constants was found to be 25 kcal. per mole.

TABLE III

THE EXCHANGE OF SODIUM IODIDE WITH *m*-NITROIODOBENZENE

Temp. °C.	Reactant conc., molarity		Maximum exchange, %	$k \times 10^4$ liter-mole^{-1} hr.$^{-1}$	$k \times 10^4$ hr.$^{-1}$
	NaI	m-$NO_2C_6H_4I$			
238	0.037	0.368	89	826	30.4
	0.074	0.368	77	543	39
	0.147	0.147	37	220	32*
207	0.038	0.382	67	107	4.1
	0.076	0.382	55	59.7	4.6
	0.153	0.153	18	29	4.5*
185	0.039	0.394	60	33	1.32
	0.079	0.394	33	14.2	1.12
	0.158	0.158	19	9.4	1.4*
157**	0.041	0.410	14	5.4	0.2
	0.082	0.410	12	4.1	0.35
	0.164	0.164	3.5	1.8	0.3

* *Analyses for gain in activity of aromatic iodide.*
** *Only one value of k at each concentration was obtained.*

Exchange of Sodium Iodide with Iodobenzene

Results for the exchange of sodium iodide with iodobenzene are shown in Table IV. At 238°C., free iodine was observed in all samples, as well as small amounts of a black precipitate. The results at 157°C. are only approximate, owing to the small percentage exchange. First order velocity constants cal-

TABLE IV

THE EXCHANGE OF SODIUM IODIDE WITH IODOBENZENE

Temp. °C.	Reactant conc., molarity		Maximum exchange, %	$k \times 10^4$ liter-mole^{-1} hr.$^{-1}$	$k \times 10^4$ hr.$^{-1}$
	NaI	C_6H_5I			
238	0.037	0.662	88	240	8.9
	0.074	0.662	74	148	10.9
	0.147	0.294	18	33	5.0
207	0.038	0.688	48	20.5	0.79
	0.076	0.688	42	14.3	1.1
	0.153	0.306	14	5.6	0.86
185	0.039	0.719	22	5.7	0.22
	0.079	0.719	11	2.5	0.20
	0.158	0.315	6	1.8	0.25
157	0.041	0.736	2.7	0.44	0.018
	0.082	0.736	3.4	0.5	0.04
	0.164	0.328	2.9	0.6	0.10

culated on the assumption that the rate was independent of sodium iodide concentration (last column) give a much better representation of the behavior with varying concentrations than do the second order constants. The variation with temperature of the first order constants corresponds to an activation energy of 24 kcal. per mole.

Comparison of the rates in normal reaction mixtures with those for similar mixtures to which small amounts of iodine (5×10^{-5} gm.) were deliberately added showed that the presence of iodine accelerated the reaction 10–15%. The presence of water (0.5 gm.) retarded the reaction, as did also the presence of sodium sulphite, to the extent of about 15%.

These results indicate that the formation of free iodine during reaction may lead to values of the rate constant that are too large. However, no significant increase in k with time was observed in any of the experiments where free iodine was formed, perhaps because the amount formed was too small to cause a detectable effect.

Discussion

The exchange reactions involving *o*- and *p*-nitroiodobenzenes, in the temperature range of approximately 170°–238°C., may be satisfactorily interpreted as bimolecular reactions between the aromatic iodide and iodide ion. In the same temperature range, however, it appears that the comparable reactions of *m*-nitroiodobenzene and iodobenzene must be regarded as involving a first order rate-controlling step, independent of the sodium iodide concentration. The same may well be true for the *o*- and *p*-nitroiodobenzene reactions at lower temperatures.

It does not seem possible to offer a satisfactory explanation of the first order kinetics in the two systems where such behavior apparently prevails. A rate-controlling ionization of the aromatic iodide is improbable from theoretical considerations (3), while there is no direct evidence for a homolytic fission to produce free radicals, a process that would not be favored in the highly polar solvent used (10, p. 15). Further study of analogous systems might enable an opinion to be expressed on this matter.

The difference in behavior between *o*- and *p*-nitroiodobenzene on one hand and *m*-nitroiodobenzene and iodobenzene on the other is presumably the result of differences in electron density at the site of reaction. A substituent group affects this electron density by inductive and resonance effects. A nitro group in the ring confers electropositivity to the carbon atom bonded to iodine in the order ortho > para > meta. The approach of a negative iodide ion should therefore be facilitated in the order ortho > para > meta, and the activation energy of the corresponding second order reactions should increase in the same order. In the present study, the two reactions that are second order behave as expected. With *m*-nitroiodobenzene and the unsubstituted iodobenzene, second order behavior apparently is not observable, even at 238°C.

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THE SYNTHESIS OF SOME STEREOISOMERIC DERIVATIVES OF DECAHYDRONAPHTHALENE[1]

By A. Zlatkis[2] and E. A. Smith

Abstract

Both racemic forms of *trans* 2-chlorodecalin have been prepared and separated in pure form. The reaction between these chlorodecalins and ethylmagnesium bromide has been studied and two racemates of *trans* 2-ethyl decalin have been isolated. Some progress has been made in the preparation of the 9-chlorodecalins. A new method for converting *cis* decalin to *trans* decalin rapidly in high yield using tertiary butyl chloride and anhydrous aluminum chloride is indicated.

Introduction

The preparation of the monoalkyl derivatives of decahydronaphthalene (decalin) has not been extensively investigated. One approach to the synthesis of this group of hydrocarbons has been the hydrogenation of the corresponding naphthalene derivative. Three isomers of 1-methyldecalin have been prepared in this manner (9).

The present work describes a new route by way of the reaction of the monochlorodecalins with ethylmagnesium bromide. The two racemic forms of *trans* 2-ethyldecalin have been prepared from the corresponding chlorodecalins.

Experimental*

Preparation of trans Decalin

Commercial decalin (Eastman Kodak Co.) (500 ml.) was treated twice with 200 ml. of concentrated sulphuric acid with vigorous agitation. The purified product was then dried for 24 hr. over sodium hydroxide pellets. Refractometric measurements indicated that the decalin contained 70% of the *cis* isomer and 30% of the *trans* isomer (8).

The conversion of *cis* to *trans* decalin in the presence of anhydrous aluminum chloride has been reported by Zelinsky (10), who obtained low yields. It was found since by the author that by using a 10% catalytic mixture of 3:1 anhydrous ferric chloride and anhydrous aluminum chloride, complete isomerization could be effected in three hours (11). Final purification of the *trans* decalin was accomplished by vacuum distillation at 10 mm. pressure through a Stedman column. The physical constants of the resultant product were: b.p.$_{10}$ 63.7°C., n_D^{20} 1.4696, d_4^{20} 0.8699. These agreed closely with those reported in the literature by Seyer and Walker (8): b.p.$_{10}$ 63.7°C., n_D^{20} 1.4697, d_4^{20} 0.8695.

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* *All boiling points are uncorrected.*

The Chlorination of trans Decalin

The procedures of Gysin (5) and Borsche and Lange (2) have been modified as follows to give higher yields.

The reaction vessel consisted of a one-liter three-necked flask. Chlorine, previously moistened by passing through a wash bottle containing water, was passed in through a tube which was pulled out to a capillary. A dropping funnel at the center of the flask permitted decalin to be dropped in slowly. The capillary part of the chlorine tube was placed 1/2 in. from the end of the dropping funnel so that an atomizing effect could be produced when the decalin and chlorine met. A glass tube extending to the bottom of the vessel and leading to a receiver, at a level below the reaction flask, acted as a siphon and captured the product.

The decalin was sprayed in the form of a fine mist, with chlorine under pressure, against the walls of the reaction vessel which was immersed in an ice–salt bath. The system was kept slightly below atmospheric pressure to prevent the escape of chlorine, and to facilitate removal of the product from the reaction vessel to the receiver. Decalin was passed through the apparatus at the rate of 100 ml. per min. The chlorinated product was recycled until the desired degree of chlorination, as determined by checks on the specific gravity, was obtained. The reaction was stopped when the specific gravity of the chlorinated product reached unity. As a rule, seven to nine cycles were required. The crude chlorodecalin was washed first with 15% sodium carbonate solution, then with water. This was dried over calcium chloride and finally distilled. Five hundred milliliters of decalin could be fully treated in one hour using this atomizing procedure, with an over-all yield of 80% or better.

The following conditions appeared to be most favorable for the reaction:
(*a*) Intimate mixture of the chlorine with the decalin,
(*b*) The use of a small amount of iodine (1/2%) as a catalyst,
(*c*) Moistening the chlorine before passing it into the reaction chamber,
(*d*) The use of a strong light source to catalyze the reaction,
(*e*) Stopping the reaction before appreciable dichlorination set in.

Distillation of the halogen products was carried out in a large fiber glass packed fractionating column (3 ft. by 1 in.) under vacuum. The still was tested at total reflux at atmospheric pressure, and gave a result of 20 theoretical plates. Several distillations were necessary to obtain the isomers in their pure forms. Table I shows the properties found for these chlorodecalins. The *trans* isomer

TABLE I

Property	*trans* 2-chlorodecalin A	*trans* 2-chlorodecalin B
b.p.$_{15}$, °C.	115	117
n_D^{20}	1.4946	1.4970
d_4^{20}	1.0234	1.0377
% C : H : Cl calc.	69.56 : 9.86 : 20.58	69.56 : 9.86 : 20.58
% C : H : Cl found	69.62 : 9.88 : 20.50	69.48 : 9.92 : 20.60

of 2-chlorodecalin corresponding to the chlorodecalin derivable from 2-decalol (m.p. 75°C.) (4) has been designated as *trans* 2-chlorodecalin A, the one derivable from 2-decalol (m.p. 53°C.) *trans* 2-chlorodecalin B.

The values found compare favorably with those of the literature (4, 6). The chlorodecalins are colorless, but turn light yellow on standing.

Twenty milliliters of *trans* 2-chlorodecalin A was heated for six hours in 25 ml. of diethyl ether in the presence of 5 gm. of magnesium, resulting in the decalylmagnesium chloride. The latter, on treatment with oxygen at 0°C. and followed by decomposition with water, resulted in the decalol m.p. 74°C. The same procedure with *trans* 2-chlorodecalin B produced the decalol m.p. 53.5°C.

Synthesis of the 9-Chlorodecalins

Bartlett's work (1) on the catalyzed exchange of hydrogen and halogen offered a convenient method of preparing a pure 9-chlorodecalin. Pure isomers of decalin were used to facilitate identification of the products.

Three hundred milliliters (1.89 moles) of pure *trans* decalin was mixed with 115 ml. (1.05 moles) of tertiary butyl chloride in a two-liter separatory funnel. To this was added 15 gm. of anhydrous aluminum chloride, and the mixture was then shaken for a period of 30 sec. A reaction took place as soon as the aluminum chloride came in contact with the solution. The solution turned dark amber in color and the sides of the vessel became black. On quenching the reaction with three times the volume of water, two layers were formed. The top oily, amber layer was washed with water and dried with phosphoric anhydride. This solution now had a blue fluorescence and on distillation gave a small yield (14%) of a 9-chlorodecalin: b.p.$_7$ 83°C., n_D^{20} 1.4937, d_4^{20} 1.0007. Calc. % Cl = 20.58. Found % Cl = 20.67.

The use of *cis* decalin in a similar procedure produced a more violent reaction and the 9-chlorodecalin yield was greater (20%). During the course of the reaction (40 sec.), the *cis* decalin had almost completely isomerized to the *trans* form. This is rather remarkable in view of the authors' earlier experience in a study of this isomerization (11). The 9-chlorodecalin from this reaction had the following properties: b.p.$_7$ 85°C., n_D^{20} 1.4946, d_4^{20} 1.0645. Found % Cl = 20.60 This was probably a mixture of *cis* and *trans* 9-chlorodecalins due to the simultaneous occurrence of the isomerization.

Dehydrohalogenation with Pyridine

In order to identify the chlorinated product obtained with *trans* decalin, the corresponding 9, 10 octalin was prepared: 20 ml. of the chlorodecalin n_D^{20} 1.4937 was refluxed in an equal volume of dry pyridine for three hours, at the end of which time a white precipitate of pyridine hydrochloride had formed. The red solution was decanted off, washed with water, then dried with phosphoric anhydride. The product was now colorless and had the following properties: b.p.$_{13}$ 74°C., n_D^{20} 1.4984. The literature reports (7) for 9, 10 octalin: b.p.$_{12}$ 75°C., n_D^{20} 1.4996. Three milliliters of the octalin was converted to the

blue nitrosochloride. A solution consisting of the octalin, 10 ml. glacial acetic acid, and 6 ml. of isoamyl nitrite was cooled to −30°C. and then treated with 6 ml. of concentrated hydrochloric acid in a dropwise manner. The resulting blue precipitate was washed with acetone and had a melting point of 90–91°C. The melting point for 9, 10 octalin nitrosochloride is reported as 92°C. in the literature (3).

Synthesis of the trans 2-Ethyldecalins

Eighty-five milliliters (0.5 mole) of the colorless *trans* 2-chlorodecalin A was added to 0.75 mole of ethylmagnesium bromide in 100 ml. of isoamyl ether over a period of one hour. The Grignard reagent had been prepared in the usual manner. After refluxing for one hour, the solution was allowed to stand overnight. The reaction mixture was then poured into a beaker containing 300 ml. of 1:1 sulphuric acid solution and about 200 gm. of chopped ice. The ether layer was distilled in a fiber glass-packed column. Although the yield was low (10%) 5 ml. of a pure product was obtained: b.p.$_8$ 70°C., n_D^{20} 1.4716, d_4^{20} 0.8583. Calc.: C, 86.64, H, 13.36%. Found: C, 86.26; H, 13.53%.

A similar procedure was followed for the preparation of the other isomer of *trans* 2-ethyldecalin. In the latter case, *trans* 2-chlorodecalin B was used. The resulting product (5 ml.) showed the following characteristics: b.p.$_8$ 72°C., n_D^{20} 1.4809, d_4^{20} 0.8803. Calc.: C, 86.64; H, 13.36%. Found: C, 86.26; H, 13.52%.

Conclusions

While the Grignard reaction with the chlorodecalins has not produced good yields in the preparation of the *trans* 2-ethyldecalins, the racemic forms of the chlorodecalins isolated are of interest for further investigation. Particular significance may be attached to the isomerization occurring when *cis* decalin was treated with tertiary butyl chloride in the presence of anhydrous aluminum chloride. The catalyzed exchange of hydrogen and halogen offers a simple, convenient method for the conversion of *cis* decalin to *trans* decalin. Complete isomerization is effected in only 40 sec.

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PARTICLE SHAPE IN THIXOTROPIC SUSPENSIONS[1]

By A. F. Sirianni, G. B. Moses, and I. E. Puddington

Abstract

Several equations have been proposed that predict the shape of suspended particles when the viscosity of a suspension of known concentration is measured. These are not applicable to suspensions showing thixotropy, owing to the dependence of the measured viscosity on the shear rate used. However, by using viscosity values that have been extrapolated to infinite rate of shear, good agreement has been found between the predicted and measured shapes for particles in thixotropic systems, and the method appears to be suitable for submicroscopic particles. A scheme is also proposed for comparing the degree of thixotropy of different systems.

When the viscosities of most homogeneous liquids are measured at different rates of shear, constant values are obtained unless the shearing is sufficiently great to cause turbulence. The same is true of suspensions provided the particles of the solid phase are sufficiently separated to avoid mutual interference. The increase in viscosity due to the suspended particles has been shown theoretically and practically to be proportional to the volume concentration. With spheres at low concentrations the proportionality factor is 2.5. As the particles depart from the spherical shape larger factors are required. The various equations that have been derived to account for the effect of the shape of the particles, their rigidity, and the effect of Brownian movement have been excellently reviewed (1, 10).

In actual suspensions, however, it is more common that the solid phase particles do interfere mutually, in many cases at low volume concentrations, and the experimental value that one obtains on measuring the viscosity is markedly dependent on the rate of shear used during the measurement. It frequently happens that the system as a whole may be a solid at zero rate of shear and yet have a viscosity only slightly higher than that of the suspension medium at high rates of shear. When this phenomenon occurs isothermally and reversibly the system is said to be thixotropic, and it is obvious that the usual equations relating viscosity and volume concentration no longer hold.

When some thixotropic suspensions are examined microscopically, the solid phase will be seen to exist in agglomerates that may be readily broken up by agitation but that re-form, enmeshing large volumes of liquid phase when left undisturbed. In some cases this re-formation is virtually instantaneous; in others considerable time may elapse before rest equilibrium is again established. It seems likely, however, that under any constant rate of shear, a steady state will be set up when the rate of formation of agglomerates due to mutual inter-

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ference of the particles will be equal to their rate of disintegration due to shear. Goodeve and Whitfield (7) have derived the following equation, based on this conception, relating viscosity and shear

$$\eta - \eta_0 = \frac{\theta}{s},$$

where η is the apparent viscosity of the system,

η_0 the residual viscosity $\left(\text{i.e., when } \frac{1}{s} = 0\right)$

s the rate of shear,

θ the coefficient of thixotropy.

From the derivation, the coefficient of thixotropy is the rate of growth of structure with time divided by the probability of the viscosity being reduced in unit time by unit shear and has the dimensions of force per unit area (dynes per cm.^{2}). It may be measured, as seen from the equation, by the limiting slope of the viscosity vs. reciprocal shear curve. The extrapolation of this curve to $\frac{1}{s} = 0$ gives the value of η_0, that is, the viscosity that the system would have at infinite shear when no thixotropy can be present. This reasoning ignores, of course, any effects peculiar to very high rates of shear that might appear if one were to attempt experimental measurements in this region.

Goodeve's theory also predicts the effect of solids concentration on θ from the following considerations: The rate of formation of thixotropic links due to any one particle will be proportional to the concentration of particles in the layer passing over it, and the number of particles forming links from the passing layer will also be proportional to the concentration. Thus the total rate of link formation will be proportional to the square of the concentration. This was actually the case for carbon black suspended in oil, as Goodeve's data show.

In an effort to get more information from the data than was contained in Goodeve's original communication, it was considered that some idea of the shape of the suspended particles should be available by examining the change in the values of η_0 with increasing solids phase concentration.

The original Einstein equation,

$$\frac{\eta}{\eta_0} - 1 = \frac{5}{2} C$$

or its extension for higher concentrations is valid only for spheres and would probably have limited application. Various other equations have been developed which contain "f" or axial ratio terms and are thus applicable to other than spherical particles. Most of these equations agree reasonably well amongst themselves provided "f" is not too high (i.e., about 50) but diverge at high axial ratios. In their derivation it is usually assumed that the particles are unoriented and are acted on by Brownian forces. While it is doubtful whether

Brownian movement is a factor under conditions of high shear, it is also doubtful if orientation exists to any great extent in particles of the shape and size about to be described, since a fluid velocity gradient across the short axis of the particle is almost certain to result in a torque. Indeed, it has recently been shown by Mason (11) that rotation actually does take place with visible particles in a shear field. In view of the lack of adequate knowledge of conditions prevailing at infinite shear, the choice of equations did not seem to be critical and the rather simple Kuhn equation

$$\frac{\eta}{\eta} - 1 = \left(\frac{5}{2} + \frac{f^2}{16}\right) C$$

was used in the present work. The values of "f" actually found using it agreed well, in the cases examined, with those obtained with the more complicated Guth and Gold equation, which was derived for moderate concentrations of rigid rods unaffected by Brownian movement, and its use seems to have been justified. In some cases where microscopy was practicable "f" could be measured directly and compared with those values found viscometrically.

Results of the application of Kuhn's equation to Arnold and Goodeve's (2) viscosity data on carbon black in oil and also to Robinson's (14) experimental results with glass spheres in oil are shown in Fig. 1. Robinson's system showed no viscosity dependence on rate of shear but Goodeve's was definitely thixotropic. In both cases "f" depends on concentration but approaches linearly a value of unity on extrapolation to zero concentration.

These results were sufficiently encouraging to warrant an extension of the investigation to highly thixotropic systems where the solid particles might be highly anisodimensional.

When applied to two independent sets of data on the viscosity of dispersions of lime soaps in hydrocarbon oil (3, 12) Kuhn's equation produced some interesting results. Arveson's data indicated a substantially constant value for "f" of 17 for 3 to 14% volume concentration of soap. Two master samples of similar dispersions were used by Moses and Puddington (12) and intermediate concentrations were obtained by dilution. One of these samples gave an "f" of 15 in the concentration range 11–16%, the other a value of 23 for 18 to 30% of soap. Comparison of these values with electron micrographs of calcium soap fibers from similar systems shows these figures to be of the correct order although the viscometrically measured "f" values would be expected to be low if appreciable shear orientation had taken place.

Two electron micrographs of soap particles from lime base greases are shown in Figs. 2 and 3. These are taken from the work of Ellis (5) and of Farrington and Birsdall (6). Fig. 2 shows the soap still dispersed in the oil while in Fig. 3 the oil has been leached out and the sample shadow cast. The obvious conclusion is reached after comparing these figures that remarkable similarity exists in the size and shape of the lime soap particles of greases from different sources where different procedures were probably used in their preparation.

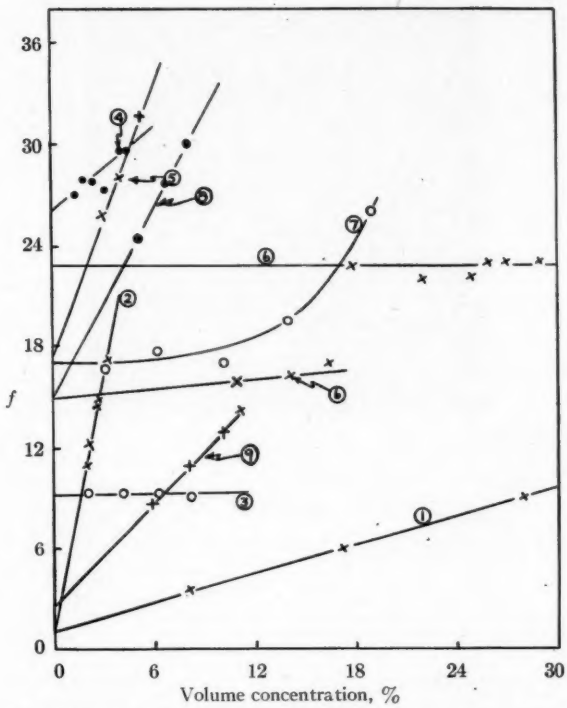

FIG. 1. *Relation between particle axial ratio and volume concentration. Curve 1, glass spheres in oil (Robinson); 2, carbon black in oil (Arnold and Goodeve); 3, rice starch in carbon tetrachloride–toluene (Hatschek and Jane); 4, silica aerogel × 0.5 in oil; 5, Shawinigan black in oil; 6, calcium soap in oil (Moses and Puddington); 7, calcium soap in oil (Arveson); 8, polythene in oil; 9, barium sulphate in oil.*

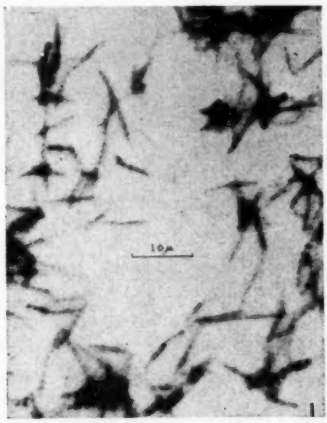

FIG. 2. *Electronmicrograph of calcium soap in oil (Ellis).*

FIG. 3. *Electronmicrograph of calcium soap petroleum ether washed and gold shadowed (Farrington and Birsdall).*

Applying this treatment to the viscosity of rice starch suspended in a hydrocarbon – carbon tetrachloride solution as measured by Hatschek and Jane (8), a constant "f" of 9 in the concentration range of 2 to 8% is found. This is surprising since rice starch particles are essentially spherical. However, there is some evidence (13) that agglomerates that are substantially spherical in the undisturbed state are first elongated on shearing, and only after very high shear rates are applied do they break down to individual particles. Absolute shear rates used in this work could not be found and it is probable that the extrapolation to $\frac{1}{s} = 0$ was made from data obtained when the agglomerates were still in the ellipsoidal shape.

Using this procedure with dispersions of Shawinigan black in hydrocarbon oil, an extrapolated "f" equal to 17 was obtained. This again seems very high, but Shawinigan black is known to form extremely tenacious chains (4) and it is quite probable that these were stable under the conditions of shear that were obtained in the capillary tube used in the measurements. The samples had been passed through a colloid mill during preparation and it is likely that the shears exerted there (about 7×10^5 sec.$^{-1}$) fixed the minimum "f" values that could be reached later in the capillary.

The results on dispersions of silica in hydrocarbon oil in concentrations of 1–4% are of special interest. The silica used in this case was an aerogel prepared from a 2% aquagel according to the method of Kistler (9). The particles are supposed to be in substantially the same condition as found in the original gel and are undoubtedly fibrillar, with a high axial ratio. The system is also highly thixotropic. Since the ultimate particles are subelectronmicroscopic no direct measurement is possible; however, the "f" values of 55–60 found are not unduly high.

Thixotropic suspensions of polyethylene were prepared by dissolving the solid in hot lubricating oil and allowing the system to cool. In concentrations of 4–8% by volume a solid of greaselike consistency was produced. Pigment grade barium sulphate in volume concentrations of 6–10% gave dispersions of similar consistency in oil. About 0.5% of water added to the latter system increased the amount of thixotropy considerably. Values of "f" obtained from viscometric measurements on these dispersions are also shown in Fig. 1. The extrapolated "f" values of 15 for polyethylene and 2–3 for barium sulphate agree well with microscopic observations.

While the data presented here are perhaps too meager to be conclusive, they certainly suggest that this approach could be of considerable value in thixotropic systems that do not lend themselves readily to microscopy.

In checking Goodeve's postulation that the coefficient of thixotropy should be proportional to the square of the solids concentration a graph was constructed and shown in Fig. 4 where the log coefficient of thixotropy is plotted against log concentration. If the postulate is correct, a straight line with a slope of 2 should result with each system. That this was the case with the data discussed above is readily seen. The figure also illustrates that it is possible to compare the degrees of thixotropy of the various systems by comparing the concentrations required to produce any selected value of θ. It also should be possible to prepare systems having a predicted value of θ from a knowledge of the properties of the system at any one concentration. It is again interesting

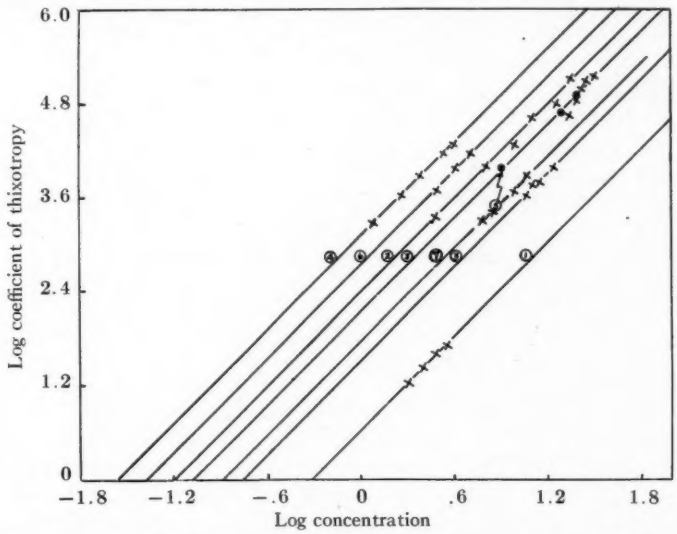

FIG. 4. *Relation between coefficient of thixotropy and concentration for suspensions in oil. Curve 1, carbon black (Arnold and Goodeve); 2, calcium soap (Arveson); 3, calcium soap (Moses and Puddington); 4, silica aerogel; 5, calcium soap (Tapp, unpublished); 6, Shawinigan black; 7, barium sulphate.*

to note the similarity in degree of thixotropy shown by the lime soap greases from several independent sources.

Such a series of curves could be of considerable practical use in correlating data on thixotropic suspensions provided that the slope of 2 is general. While there may be exceptions, this value was faithfully followed in all the data used here and the approach seems to warrant further investigation.

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HYDROGEN PEROXIDE AND ITS ANALOGUES

I. DENSITY, REFRACTIVE INDEX, VISCOSITY, AND SURFACE TENSION OF DEUTERIUM PEROXIDE - DEUTERIUM OXIDE SOLUTIONS[1]

By M. K. Phibbs and Paul A. Giguère

Abstract

Some deuterium peroxide containing less than 0.3% ordinary hydrogen was produced both by the persulphate and the electric discharge methods. By means of fractional distillation, solutions of deuterium peroxide in deuterium oxide of various concentrations up to 90% were obtained, of which the following properties were measured: refractive index at 25°C., density, viscosity and surface tension at 0°C. and 20°C. Measurements of the last two properties were also extended to solutions of ordinary hydrogen peroxide. The physical constants of the two isotopic peroxides are compared and discussed. The density, viscosity and surface tension of supercooled heavy water at 0°C. were also measured for the first time.

The deuterium analogue of hydrogen peroxide, D_2O_2, has attracted relatively little attention so far owing, no doubt, to the difficulty of obtaining it in a pure state. A number of kinetic and other investigations have been made by diluting concentrated hydrogen peroxide in various amounts of heavy water (1,2,4,5,8,12,15,21,29). Obviously this procedure yields rather complex mixtures of the following molecular species: H_2O, HDO, D_2O, H_2O_2, HDO_2, and D_2O_2. The first work dealing with substantially pure deuterium peroxide, that is, free of contamination by ordinary hydrogen, was that of Fehér (9,10,11) who prepared some 15–20 cc. of this compound by the persulphate method in order to measure its Raman spectrum. More recently Taylor (25) has reported preliminary results on the infrared absorption of the fairly pure compound in the liquid state. Now that heavy water is available in larger quantities than before, it is deemed worth while to prepare the pure isotopic peroxide in sufficient amount to enable accurate measurement of its physical properties.

Experimental Methods and Results

An important part of this project consisted in the actual preparation of the deuterium peroxide. The potassium persulphate method was first tried, since it had proved workable (11). Fehér had reported some difficulty due to frothing of the persulphate mixture on hydrolysis. With this in mind a number of improvements were effected in his original apparatus. In particular an anti-foaming device (7) was added on top of the reaction vessel. In spite of this the process remained extremely tedious and awkward to operate. Furthermore it turned out to be rather wasteful of the scarce heavy water because an appreciable portion of the deuterium is eventually transformed into potassium deuterium sulphate from which it cannot be recovered quantitatively.

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Contribution from the Department of Chemistry, Laval University, Québec, Que.

Therefore that method was soon discarded in favor of the electric discharge through water vapor (22,23). An apparatus was built in which the vapor of heavy water could be dissociated in an electrodeless discharge operating at 22 megacycles. The dissociation products were condensed in a liquid air trap. Under optimum conditions a 60% solution of deuterium peroxide in deuterium oxide was obtained which was concentrated further by fractional distillation. This part of the project will be described in a subsequent paper. The material made by both methods amounted to about 10 cc. of a 90% solution and 10 cc. of a 50% solution by weight. Although they seemed very stable these solutions were found to decompose at a rather high rate, very likely because their large surface-to-volume ratio favored the heterogeneous catalysis. To overcome that difficulty the samples were kept at low temperature, and once a solution had been prepared and analyzed, the four properties were determined in rapid succession.

The small amount of material available made it necessary to build special instruments. All glassware was thoroughly cleaned following the procedure recommended by Huckaba and Keyes (16). Contamination of the deuterium compounds by atmospheric moisture during handling was carefully avoided. A test of the liquid by means of its infrared spectrum made after the physical measurements showed no significant increase in hydrogen content over the original amount present in the heavy water used, viz., 0.25%. The peroxide content of the solutions was determined by the standard volumetric titration with permanganate using samples of about 0.1 gm.; the estimated accuracy was of the order of 1 in 1000. A constant temperature bath controlled to $\pm$ 0.05°C. was used for the measurements at 20°C. while those at 0°C. were done in a well agitated ice bath. Heavy water freezes at 3.8°C. but it supercools readily enough to enable easy measurement of its physical properties at 0°C.

Density

A U-tube type pycnometer of conventional design with a capacity of 2.9344 ml. at 20°C. was constructed for these measurements. In order to increase the accuracy of this small container the oblique arms were made of fine bore capillary tubing, 0.2 mm. radius for the inlet tube and 0.5 mm. radius for the other arm. The usual weighing corrections were neglected because of the small size of the instrument and the negligible dead space.

As in most measurements with hydrogen peroxide the accuracy was largely limited by formation of oxygen bubbles due to spontaneous decomposition. At 0°C. there was little trouble on that account but at 20°C. it was almost impossible to avoid it completely in spite of repeated cleaning of the pycnometer. After a number of trials the following procedure was adopted and found to give fairly reliable results: the filled pycnometer was allowed to reach temperature equilibrium in a bath at 20°C. Then by applying gentle pressure on one arm the excess liquid was forced out, while tapping, until the liquid level dropped to the reference mark. Thus any stray bubbles formed during

temperature equilibration were swept out of the liquid for the short time required to measure the volume of sample.

The experimental results are presented in Table I along with those for the three other properties measured. The density curves need not be reproduced here as they are closely similar to those for hydrogen peroxide. In Fig. 1 the molecular volumes of the solutions are plotted as deviation from ideal solution relationship, which is more significant for that sort of data. The value found here for the density of 99.75% pure heavy water at 20°C. is in good agreement with the most recent data, 1.1053 gm. per ml. (27,28). No data could be found in the literature for the density of the supercooled liquid but the present result, 1.1046 gm. per ml. at 0°C. falls quite closely on the density–temperature curve extrapolated below the freezing point. The values for pure deuterium peroxide (Table III) were obtained by extrapolation, a fairly accurate procedure in this case because of the very slight curvature of the density–composition (in weight %) curves. A straight line was drawn through the two higher concentration points and a small correction was applied, equal to that for the hydrogen peroxide curves which are known with good precision (14,16).

TABLE I

DENSITY, REFRACTIVE INDEX, VISCOSITY, AND SURFACE TENSION OF DEUTERIUM PEROXIDE SOLUTIONS

D_2O_2		d_4^t, (gm./ml.)		n_D	η centipoises		γ, dynes/ml.	
Weight %	Mole %	0°C.	20°C.	25°C.	0°C.	20°C.	0°C.	20°C.
0.00	0.0	1.104_6	1.105_6	1.32806	2.35_0	1.24_4	76.1	73.3
9.05	5.24	1.141_4	1.137_0	1.3340	2.23_0	1.25_5	76.5	73.5
20.02	12.22	1.185_7	1.178_0	1.3414	2.18_4	1.26_3	77.0	74.1
33.6_8	22.0_3	1.244_0	1.232_0	1.3510	2.18_2	1.30_0	77.9	75.2
43.2_5	29.7_9	1.286_0	1.270_1	1.3579	2.19_3	1.32_6	78.7	75.8
56.6_8	42.1_3	1.344_7	1.328_4	1.3678	2.19_2	1.37_2	79.8	77.0
73.7_8	61.0_2	1.423_6	1.403_3	1.3809	2.14_9	1.39_7	81.4	78.7
91.6_5	85.9_3	1.513_0	1.490_8	1.3955	2.04_7	1.37_9	82.7	80.0

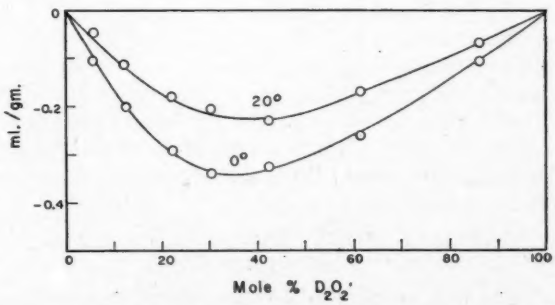

Fig. 1. Deviation from a straight line of molecular volume of D_2O_2–D_2O mixtures at 0° and 20°C.

Refractive Index

The measurements were made with a Precision Abbé Refractometer (Bausch and Lomb), the technique being generally the same as previously reported for hydrogen peroxide solutions (13). These measurements required very small samples, one drop or two of liquid, which was fortunate since no recovery was possible, contrary to the other three properties. Measurements at another temperature besides 25°C. were not possible with the time and material available. It is hoped they can be completed in the near future in view of the great convenience of this method for analyzing solutions of deuterium peroxide. In addition to the small amount of liquid needed, the refractive index can be measured very quickly and it is less affected by slight decomposition than most other physical properties.

The plot of deviation from a straight line, Fig. 2, shows that the measurements were internally as consistent as those for hydrogen peroxide solutions. The refractive index of heavy water was taken from the literature (19) as it fell beyond the range of the instrument used; that of pure D_2O_2 is based on extrapolation as described under 'density'.

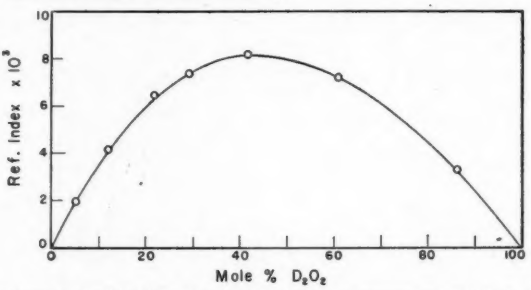

Fig. 2. Deviation from a straight line of refractive index measurements of D_2O_2–D_2O mixtures at 25°C.

Viscosity

An Ostwald type viscometer of small dimensions was made according to the specifications of Cannon and Fenske (3). The upper bulb had a volume of about 1 cc., and a determination could easily be made with 3 cc. of liquid. The instrument was so designed that no surface tension correction was necessary; the capillary was fine enough so that flow times were always greater than 180 sec. and the kinetic energy corrections were negligible. The viscometer was calibrated with pure water at 20°C. For measurements on the same volume (3cc.) of liquid at 0°C. it was necessary to correct for the change of driving head due to contraction of the liquid on cooling. This correction was calculated from the formula:

$$C_{t_2} = C_{t_1}\left[1 - \frac{(V_2 - V_1)}{0.785\ Hd^2}\right],$$

where C is the viscometer constant at the two temperatures, V the volume of liquid sample, d the diameter of the lower bulb in centimeters and H the mean

driving head in the same units. In fact the correction amounted only to 2–4 units in the fourth decimal place. The viscosity measurements were not appreciably affected by the presence of a few minute bubbles in the peroxide solution as was shown by the following checks: It was found that after degassing a solution the formation of bubbles was delayed long enough to allow a viscosity determination to be made. In all cases the results agreed quite well whether or not this precaution was taken.

The curves in Fig. 3 are based on extrapolated values for 100% deuterium peroxide and on the results of actual determinations for heavy water. The latter agree very well with those of Lewis and McDonald (18): 1.26 centipoises at 20°C. and 2.35 cp. (by extrapolation) for the supercooled liquid at 0°C. In that connection the more recent data of Lemonde (17) appear to be in error as they lead, on extrapolation, to a much higher value, 2.75 cp. at 0°C. Indeed, if his results are plotted in the form log η vs. $1/t$ there is a sharp break at 8°C.; above that temperature the curve extrapolates to 2.38 cp. at 0°C.

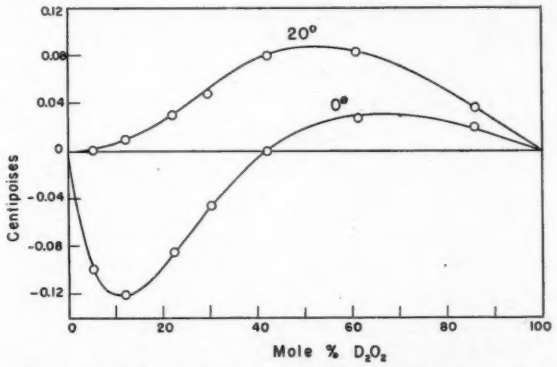

Fig. 3. Deviation from a straight line of viscosity determinations of D_2O_2 solutions at 0° and 20°C.

Since the necessary material was available the viscosity measurements were extended to hydrogen peroxide solutions over the whole concentration range. The results at 0°C. (Table II) confirm generally those of Maass and Hatcher (20), the only ones to be found in the literature, although their noted discontinuities in the viscosity–composition curves have now disappeared (Fig. 4). The present values are believed to be more accurate owing to the availability of purer hydrogen peroxide and to the revision in the viscosity constant of water, 1.798 cp. instead of 1.778 at 0°C.

Surface Tension

Measurements of this property were hindered more seriously than the others by the small volume of solutions available; they were also more sensitive to the slightest bubble formation in the liquid. The capillary rise method was applied, the above described viscometer serving for this purpose as well. This was possible because of the careful selection and calibration (by means of a

TABLE II

VISCOSITY AND SURFACE TENSION OF HYDROGEN PEROXIDE SOLUTIONS

Weight % H_2O_2	η, centipoises		Weight % H_2O_2	γ, dynes/cm.	
	0°C.	20°C.		0°C.	20°C.
0.00	1.792	1.005	0.00	75.65	72.75
8.68	1.746	1.011	17.05	76.36	73.41
19.06	1.746	1.045	26.31	76.95	74.12
25.11	1.783	—	37.33	77.69	74.67
37.3_3	—	1.120	49.7_6	78.41	75.68
42.7_2	1.844	1.140	64.3_3	79.62	76.65
49.0_8	—	1.170	71.5_5	80.48	77.36
51.9_3	1.884	—	84.1_2	81.92	78.61
62.3_7	1.917	1.219	95.7_5	82.93	79.87
69.7_8	—	1.234	97.8_8	82.81	79.88
71.5_5	1.933	—	——	——	——
81.2_1	1.919	1.266	——	——	——
91.7_6	—	1.262	——	——	——
95.7_5	1.854	1.259	——	——	——
100.0	1.819	1.249	——	——	——

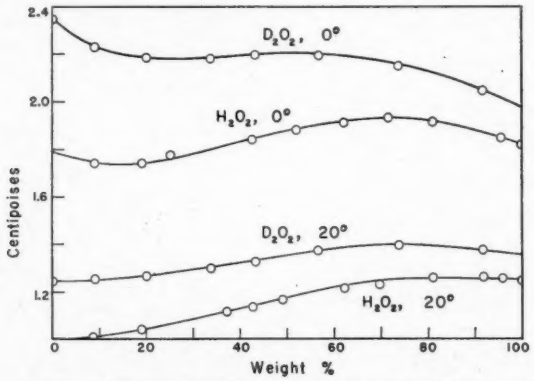

Fig. 4. Viscosity at 0° and 20°C. of H_2O_2–H_2O and D_2O_2–D_2O mixtures.

mercury index) of the capillary, a Tru-Bore tube with a remarkably constant radius: 0.1976 ± 0.0002 mm. over the usable section. This apparatus could not give absolute measurements of surface tension, however, because of the small section of the reference surface, 1 cm. Calibration was done with distilled water, the obvious choice in this case, since its surface tension at 20°C. is almost exactly the same as that of heavy water, and that of the peroxide solutions is of the same order of magnitude. The value found for heavy water at 0°C. is again in good agreement with extrapolation of other data found in the literature (6, 26). On the other hand the limited accuracy of the present measurements, especially with concentrated solutions, render the extrapolated value for the surface tension of 100% deuterium peroxide less accurate than the other three properties, as shown in Fig. 5.*

**This plot, as well as those in Fig. 2 and 3, has no particular significance other than showing the internal consistency of the measurements.*

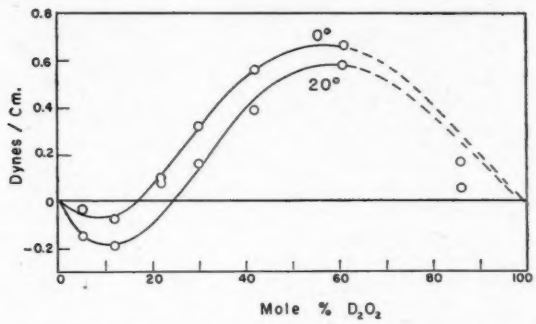

Fig. 5. Deviation from a straight line of surface tension measurements of D_2O_2 solutions at 0° and 20°C.

By analogy with water and heavy water one would expect the two isotopic peroxides to have nearly the same surface tension. In this respect the present results for deuterium peroxide are completely at odds with those of Maass and Hatcher (20). To check this point the surface tension of hydrogen peroxide solutions was measured at 0° and 20°C., again by the capillary rise method but with a much larger reference surface (30 cm.^{2}). The results shown in Table II are appreciably higher than the previous ones, which is easily understood since, for their pioneer work, Maass and Hatcher had to start with an impure and very dilute solution (3%) and mere traces of most impurities would lower the surface tension appreciably. In the present investigation, even with pure 90% hydrogen peroxide available as starting material, only erratic results were obtained at first. This was eventually traced to the presence in the commercial peroxide of some surface active agent arising apparently from the plastic material used for stopping containers. Repeated distillations were not sufficient to remove completely all traces of this impurity. Only by use of uncontaminated peroxide and glassware could consistent results be obtained.

Discussion

By way of discussion the physical properties of the two peroxides may be compared. As illustrated by the various constants in Table III substitution of hydrogen by deuterium generally has the same kind of effect on peroxide as on water molecules. Although the accuracy of the density data for the peroxides is not very high the slight increase in molecular volume on substitution seems genuine. In water this effect is interpreted as due to greater association of D_2O (24) since, as is well known, association of water molecules leads to a more open structure. Hydrogen peroxide shows no such anomalous behavior but the above mentioned effect is certainly related to association; indeed, the molecular volume of unassociated liquids is scarcely affected by deuterium substitution. In order to learn more about that question the infrared spectrum of deuterium peroxide is now being studied in this laboratory.

TABLE III

PHYSICAL CONSTANTS

	H_2O	D_2O	H_2O_2	D_2O_2
Molecular weight	18.015	20.028	34.015	36.028
Density, d_4^0	0.99987	1.1046	1.4730	1.5574
Density, d_4^{20}	0.99823	1.1056	1.4502	1.5343
Molecular volume, $(V)^0$	18.02	18.13	23.09	23.13
Molecular volume, $(V)^{20}$	18.05	18.12	23.45	23.48
Refractive index, n_D^{25}	1.33251	1.32806	1.4067	1.4026
Specific refraction, r_D^{25}	0.2054	0.2029	0.2460	0.2438
Molecular fraction, $[R]$	3.712	3.680	5.764	5.746
Polarizability, $\alpha \times 10^{24}$	1.472	1.459	2.286	2.279
Average molecular radius, in Å	1.14	1.13_5	1.32	1.32
Viscosity, η^0	1.798	2.35	1.819	1.975
Viscosity, η^{20}	1.005	1.25	1.219	1.358
Surface tension, γ^0	75.6	76.15	83.3	83.6
Surface tension, γ^{20}	72.75	72.73	80.2	81.2
Parachor	52.7	52.9	70.0	70.4

As in the case of water the decrease in molecular refraction and polarizability is indicative of tighter binding in D_2O_2 than in H_2O_2. A glance at Fig. 4 reveals that viscosity is considerably affected by isotopic substitution, in the same way as it is by temperature changes. It is easily understood why an increase of mass has the same effect as a lowering of temperature. Because of its lower zero-point energy the deuterium compound must be brought to a higher temperature than the hydrogenic compound in order to be in an equivalent situation as far as molecular motion is concerned. For the same reason the melting point of D_2O_2 should be higher than that of H_2O_2. Finally no real significance can be attached to the difference in surface tension because the values for D_2O_2 are too uncertain, as explained above.

Acknowledgment

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Résumé

A partir d'eau lourde à 99.7% de pureté l'on a préparé des solutions de peroxyde de deutérium, D_2O_2, par voie chimique (hydrolyse du persulfate de potassium) et par voie physique (décharge électrique à haute fréquence). Cette dernière méthode s'est avérée supérieure à l'autre tant par la simplicité d'opération que par le rendement. Les solutions ont été purifiées et concentrées par distillation et l'on en a mesuré l'indice de réfraction à 25°, la densité, la viscosité et la tension superficielle à 0° et 20° en fonction de la teneur en peroxyde. On a également repris les mesures de viscosité et de tension superficielle des solutions de peroxyde d'hydrogène. Les résultats obtenus conduisent à des considérations intéressantes sur les effets de la substitution de l'hydrogène par le deutérium dans des molécules simples.

THE SYNTHESIS AND ULTRAVIOLET SPECTRA OF SOME PYRAZOLONES[1]

By Paul E. Gagnon, Jean L. Boivin,[2] Paul A. Boivin,[3] and R. Norman Jones

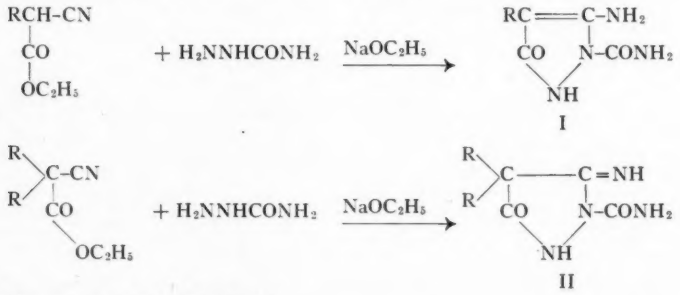
Abstract

Twenty-five pyrazolones were prepared by reacting mono- or disubstituted cyanoacetic esters with hydrazine, phenylhydrazine and semicarbazide. 4-Benzyl-3-amino-1-phenyl-5-pyrazolone has been synthesized and its properties have been compared with those of the corresponding 2-phenylpyrazolone derivative. The ultraviolet absorption spectra of several pyrazolones have been determined.

Introduction

The investigation of the reaction of ethyl cyanoacetate with hydrazine and hydrazine derivatives has been reviewed in earlier publications (2, 3, 4). Gagnon, Savard, Gaudry and Richardson (4) have studied the behavior of substituted cyanoacetic esters with hydrazine and observed that crude substituted cyanoacethydrazides yielded 4-substituted-3-amino-5-pyrazolones in excellent yield. Later, Gagnon, Boivin and Jones (2, 3) reinvestigated this transformation and prepared several 4-monosubstituted-3-amino-5-pyrazolones and 4, 4-disubstituted-3-amino-5-pyrazolones. They also synthesized some 4-monosubstituted-3-amino-2-phenyl-5-pyrazolones and 4, 4-disubstituted-3-imino-2-phenyl-5-pyrazolones.

In the present work, the preparation of other 4-monosubstituted-3-amino-5-pyrazolones and 4-monosubstituted-3-amino-2-phenyl-5-pyrazolones is described. A new series of 4-monosubstituted-3-amino-2-carboxamido-5-pyrazolones (I) and 4, 4-disubstituted-3-imino-2-carboxamido-5-pyrazolones (II) have also been synthesized by the method of Conrad and Zart (1).



I

II

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This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.
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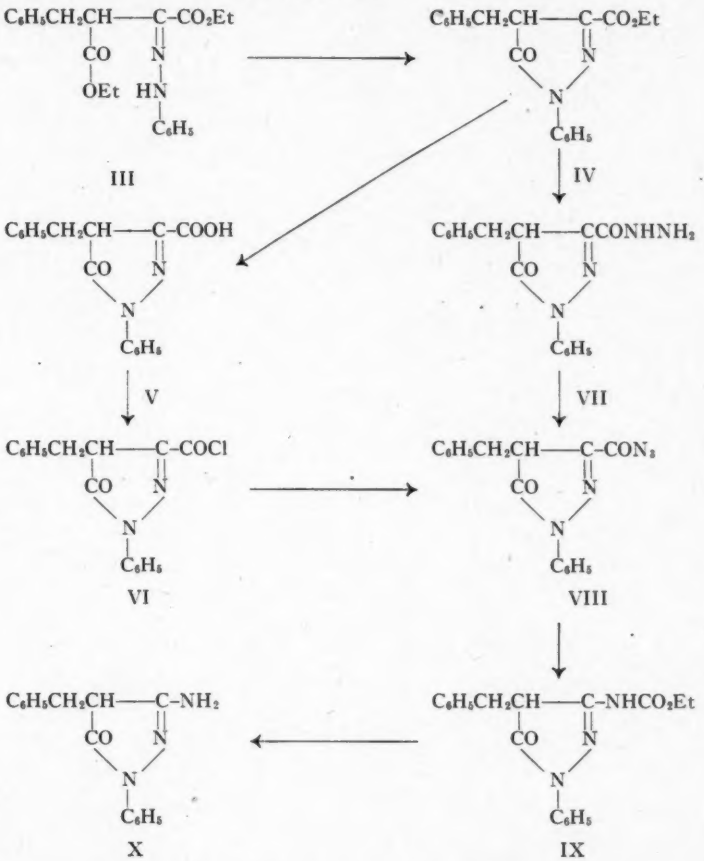
The position of the N-phenyl group in the phenylpyrazolones has been established and it has been shown that the reaction of phenylhydrazine with substituted cyanoacetic esters under the conditions described yielded 2-phenylpyrazolones, whereas unsubstituted cyanoacetic ester yielded 1-phenyl derivatives (6).

The position of the phenyl group was established by the following synthesis in which a representative 4-substituted-3-amino-1-phenyl-5-pyrazolone was prepared according to the following scheme:



Benzyl oxalacetic ester was heated with phenylhydrazine to prepare the phenylhydrazone of the ethyl ester of benzyloxalacetic acid (III), which was transformed into 4-benzyl-3-carbethoxy-1-phenyl-5-pyrazolone (IV) in an almost quantitative yield (5). The conversion of the carbethoxy group into an amino group (X) was effected through the hydrazide (VII), azide (VIII) and urethane (IX) by the Curtius degradation.

However, since the hydrazide could not be isolated in the crystalline state, the urethane was obtained also by another method. The Wislicenus pyrazolone (IV) was boiled in alcoholic potash to give the 3-carboxyl derivative (V). This acid was transformed into the acid chloride (VI) by means of thionyl chloride. The resulting crude acid chloride was treated with sodium azide to give the corresponding azide (VIII) which after treatment with ethanol yielded the same urethane (IX). This was identified by a mixed melting point determination with the sample previously obtained.

The methods outlined above for the synthesis of 4-benzyl-3-amino-1-phenyl-5-pyrazolone leaves no doubt as to the position of the phenyl group. Moreover, the melting point of this pyrazolone, 206–207°C., is much higher than that of the corresponding 2-phenylpyrazolone, 160–161°C. (2).

Derivatives of both the 1-phenyl- and 2-phenylpyrazolones were prepared. The two 3-benzoylamino derivatives obtained also had melting points differing by some 30 degrees.

By analogy to the phenylhydrazine reaction with substituted cyanoacetic esters, it may be presumed that semicarbazide will react in the same manner. This implies that the carboxamido group of pyrazolones just reported above (I and II) is in position 2.

Experimental*

Starting Materials

Ethyl α, α-Disubstituted-α-cyanoacetates

To a cooled solution of sodium ethoxide (400 ml. of absolute alcohol and one mole of sodium) a half equivalent of ethyl cyanoacetate and one equivalent of organic halide were added. The mixture was boiled under reflux on a water bath until it was neutral to litmus paper. The alcohol was removed by distillation and the residue poured into cold water and extracted with ether. The ethereal solution was washed with 5% sodium hydroxide solution to remove the mono-substituted esters, dried over anhydrous sodium sulphate, evaporated, and the residue fractionally distilled under reduced pressure.

The properties and yields of the disubstituted esters are summarized in Table I.

TABLE I

ETHYL α, α-DISUBSTITUTED CYANOACETATES, $RR(CN)COOC_2H_5$

R	Starting material	Yield, %	B.p., °C.	Formula	Nitrogen, %	
					Calc.	Found
2-Pentyl	$C_5H_{11}Br$	50	153–156 (13 mm.)	$C_{15}H_{27}O_2N$	5.53	5.60
n-Hexyl	$C_6H_{13}Br$	50	176–178 (13 mm.)	$C_{17}H_{31}O_2N$	5.00	4.92
n-Heptyl	$C_7H_{15}Br$	51	198–201 (13 mm.)	$C_{19}H_{35}O_2N$	4.53	4.52
n-Octyl	$C_8H_{17}Br$	48	152–155 (6 mm.)	$C_{21}H_{39}O_2N$	4.16	4.22
n-Nonyl	$C_9H_{19}Br$	45	170–174 (6 mm.)	$C_{23}H_{43}O_2N$	3.83	3.89

* *All melting points are uncorrected.*

Ethyl α-Cyano-α-cinnamylacetate

Ethyl cyanoacetate (113 gm.; 1 mole) and cinnamyl bromide (98.5 gm.; 0.5 mole) were added to a solution of sodium (11.5 gm.; 0.5 mole) in absolute alcohol (200 ml.). The mixture was refluxed on a steam bath for two hours. After removal of the alcohol the product was shaken with water and ether, and the dried ethereal extract evaporated and fractionally distilled under reduced pressure: b.p. 206° to 208°C. (12 mm.). Yield, 68.7 gm. (60%). Calc. for $C_{14}H_{15}O_2N$: N, 6.11%. Found: N. 6.00%.

α-Cyano-α-cinnamylacetic Hydrazide

Ethyl α-cyano-α-cinnamylacetate (22.9 gm.; 0.1 mole) was stirred with hydrazine hydrate (5.0 gm. of 100%). The two layers disappeared with evolution of heat, and after five minutes a white solid was formed. It was recrystallized from ethanol: m.p. 94° to 95°C. Yield, quantitative. Calc. for $C_{12}H_{13}ON_3$: N, 19.5%. Found: N, 19.2%.

4-Monosubstituted-3-amino-5-pyrazolones

These pyrazolones were prepared by treatment of the corresponding substituted cyanoacethydrazides with strong alkalies (2).

4-Monosubstituted-3-amino-2-phenyl-5-pyrazolones

Three compounds were synthesized by heating the substituted cyanoacetic esters with phenylhydrazine in the presence of sodium ethylate (2).

4-Monosubstituted-3-amino-2-carboxamido-5-pyrazolone

This pyrazolone was prepared by a method similar to that outlined above for the 4-monosubstituted-3-amino-2-phenyl-5-pyrazolones, except that semicarbazide hydrochloride was used instead of phenylhydrazine and the time of heating in an oil bath was 18 hr.

This compound was soluble in alkalies and strong acids. It is insoluble in sodium carbonate and can be precipitated from its alkaline solution by carbon dioxide.

4, 4-Disubstituted-3-imino-2-carboxamido-5-pyrazolones

To a solution of sodium ethoxide (0.3 mole of sodium and 120 ml. of absolute ethyl alcohol) a mixture of ethyl disubstituted cyanoacetates (0.1 mole) and semicarbazide hydrochloride (0.1 mole) was added. The reaction mixture was heated at 160°C. in an oil bath for 24 hr. The solvent was removed under reduced pressure, the residue dissolved in hot water (100 ml.) and extracted with ether to remove unchanged esters. A viscous product separated on acidification with acetic acid and soon solidified. The products were recrystallized from ethanol or acetic acid.

The pyrazolones were soluble in alkalies and insoluble in strong acids. They can be precipitated from their alkaline solution by means of carbon dioxide.

The physical constants and elemental analyses are given in Table II.

TABLE II

PROPERTIES OF INDIVIDUAL PYRAZOLONES

Compound	Formula	M.p., °C.	Analysis %		Ultraviolet absorption maxima			
			Nitrogen		Neutral‡		Acid+	
			Calc.	Found	Å	log E_m	Å	log E_m
4-Monosubstituted-3-amino-5-pyrazolones								
4-(*n*-Nonyl)-	$C_{12}H_{23}ON_3$	222–223	18.7	18.5	2840	3.58	2770	3.59
4-(*n*-Stearyl)-	$C_{19}H_{37}ON_3$	200–202	13.0	12.7	2830	3.56	2760	3.57
4-(β-Cyclohexyl-ethyl)-	$C_{11}H_{19}ON_3$	203–205	20.1	20.1	2840	3.57	2770	3.59
4-Cinnamyl	$C_{12}H_{13}ON_3$	198–200	19.5	19.3				
4-Monosubstituted-3-amino-2-phenyl-5-pyrazolones								
4-(*n*-Nonyl)-	$C_{18}H_{27}ON_3$	167–168	14.0	13.8	2680			
4-Acetyl	$C_{11}H_{11}O_2N_3$	217–219	19.4	19.6	2490	4.33	2600	4.28
4-(β-Cyclohexyl-ethyl)-	$C_{17}H_{23}ON_3$	154–155	14.7	14.4	2500			
4-Monosubstituted-3-amino-2-carboxamido-5-pyrazolone								
4-(α-Naphthyl)-	$C_{14}H_{12}O_2N_4$	273–275	20.9	20.6	2910	3.80	2920	3.80
					2810	3.96	2810	3.96
					2710	3.88	2710	3.89
					2240	5.04	2240	5.04
4-Disubstituted-3-imino-2-carboxamido-5-pyrazolones								
4, 4-Dipropyl	$C_{10}H_{16}O_2N_4$*	304–307	24.3	23.9	2880	3.98	2800	4.11
					2680	3.95		
					2340	4.24		
4, 4-Dibutyl	$C_{12}H_{22}O_2N_4$†	278–280	22.0	21.8	2860	3.96	2800	4.09
					2700	3.94		
					2360	4.31		
4, 4, *bis*-(2-Pentyl)-	$C_{14}H_{26}O_2N_4$	300	19.9	19.9	2880	3.94	2820	4.08
					2690	3.89		
					2360	4.26		
4, 4-Diamyl	$C_{14}H_{26}O_2N_4$	273–275	19.9	19.6	2880	3.96	2800	4.13
					2700	3.93		
					2340	4.44		
4, 4-Dihexyl	$C_{16}H_{30}O_2N_4$	261–263	18.1	18.5	2900	3.89	2800	4.06
					2700	3.86		
					2340	4.13		
4, 4-Diheptyl	$C_{18}H_{34}O_2N_4$	270–272	16.6	17.0	2880	3.93	2820	4.06
					2700	3.91		
					2360	4.21		
4, 4-Dioctyl	$C_{20}H_{38}O_2N_4$	266–268	15.3	15.8	2880	3.93	2820	4.07
					2700	3.91		
					2360	4.22		
4, 4-Dinonyl	$C_{22}H_{42}O_2N_4$	259–261	14.2	14.8	2880	3.93	2810	4.06
					2690	3.90		
					2350	4.19		

* *Calc. C, 53.1%; H, 8.00%. Found: C, 53.0%; H, 8.10%.* † *Calc. C, 56.7%; H, 8.66%. Found: C, 56.5%; H, 8.80%.*

‡ *Solvent, 95% ethanol.*

+ *0.1N HCl in 95% ethanol.*

4-Benzyl-3-carbethoxy-1-phenyl-5-pyrazolone (*IV*)

This pyrazolone was obtained by the method described by Wislicenus (5), but since the yield was low it was prepared also by another method. To the ethyl ester of the benzyloxalacetic acid (27.8 gm.; 0.1 mole) was added phenylhydrazine (10.8 gm.; 0.1 mole). Reaction occurred with evolution of heat. To complete the reaction, the mixture was warmed on a steam bath for one hour; during this time water was liberated. The temperature of the bath was gradually raised to 210°C. when ethyl alcohol was evolved. The solid residue was recrystallized from a large volume of ethanol: m.p. 194° to 195°C. (yield 95%).

4-Benzyl-3-carboxyl-1-phenyl-5-pyrazolone (*V*)

4-Benzyl-3-carbethoxy-1-phenyl-5-pyrazolone (32.2 gm.; 0.1 mole) was heated on a steam bath with alcoholic potash for one hour. The product was poured into ice water (600 ml.) and the solution treated with an excess of hydrochloric acid (50%). The white precipitate that separated was recrystallized from ethanol: m.p. 233° to 234°C. When the hydrolysis was attempted with an aqueous potassium hydroxide solution, the starting material was recovered. Calc. for $C_{11}H_{14}O_3N_2$: N, 9.52%. Found: N, 9.60%.

4-Benzyl-3-chlorocarbonyl-1-phenyl-5-pyrazolone (*VI*)

4-Benzyl-3-carboxyl-1-phenyl-5-pyrazolone (29.4 gm.; 0.1 mole) was added to an excess of thionyl chloride (28 ml.) and the solution heated on a water bath for one hour. The excess of thionyl chloride was evaporated under reduced pressure, leaving the 4-benzyl-3-chlorocarbonyl-1-phenyl-5-pyrazolone as a brown viscous liquid.

4-Benzyl-3-carbohydrazide-1-phenyl-5-pyrazolone (*VII*)

4-Benzyl-3-carbethoxy-1-phenyl-5-pyrazolone (16.1 gm.; 0.05 mole) was heated with an excess of hydrazine hydrate (16 ml.) at 140°C. for six hours. There was liberation of ethanol. The product was poured into water (400 ml.), and the solution neutralized with acetic acid. A white solid was obtained consisting of unreacted ester. To eliminate impurities, the solid was dissolved in concentrated hydrochloric acid at 0°C. The hydrazide passed into solution leaving a residue of insoluble starting material. The acid filtrate was neutralized at 0°C. with sodium hydroxide solution (5%). The brown resinous material, which was very soluble in alcohol, ether, and benzene, could not be crystallized.

4-Benzyl-3-carboxazide-1-phenyl-5-pyrazolone (*VIII*)

The solution of the 4-benzyl-3-carboxhydrazide-1-phenyl-5-pyrazolone in hydrochloric acid was extracted with ether to eliminate impurities. Then, it was covered with ether (200 ml.). At the beginning, it was observed that the ether layer was clear and colorless. The mixture was cooled at 0°C. and mechanically stirred while adding dropwise an aqueous solution of sodium nitrite for two hours. The 4-benzyl-3-carboxazide-1-phenyl-5-pyrazolone passed immediately

into the ether layer, which became green. The ether was decanted and the aqueous solution extracted three times with ether. The extracts were washed with sodium carbonate, dried over anhydrous sodium sulphate and poured into absolute alcohol (200 ml.). A portion of the ethereal solution was evaporated to dryness. A crystalline residue of 4-benzyl-3-carboxazide-1-phenyl-5-pyrazolone was obtained: m.p. 134°C. (with deflagration).

4-Benzyl-3-carbethoxyamino-1-phenyl-5-pyrazolone (*IX*)

This pyrazolone was obtained in two ways: (*a*) from 4-benzyl-3-chlorocarbonyl-1-phenyl-5-pyrazolone (VI) and (*b*) from 4-benzyl-3-carboxazide-1-phenyl-5-pyrazolone (VIII).

(*a*) A solution of 4-benzyl-3-chlorocarbonyl-1-phenyl-5-pyrazolone (20 gm.) in ether (300 ml.) was added to a solution of sodium azide (20 gm.) in water (30 ml.) The mixture was cooled at 0°C. and mechanically stirred in an ice bath for two hours. The ether layer was decanted, washed with sodium carbonate, and finally with ice water. The green ethereal solution was dried over anhydrous sodium sulphate and poured into absolute ethanol. The ether was distilled off with liberation of nitrogen and the alcoholic solution was heated to boiling for 12 hr. The solution was cooled overnight, when a crystalline solid separated out. It was recrystallized from ethanol: m.p. 178° to 179°C. Calc. for $C_{19}H_{19}O_3N_3$: N, 12.5%. Found: N, 13.0%.

(*b*) A solution of 4-benzyl-3-carboxazide-1-phenyl-5-pyrazolone in a mixture of ethanol and ether was heated in a flask with a fractionating column; the ether distilled off and the alcoholic solution heated to boiling for 12 hr. The solution was concentrated and a solid separated out. It was recrystallized from ethanol: m.p. 178° to 179°C. A mixed melting point of this product with the urethane above described showed no depression.

4-Benzyl-3-amino-1-phenyl-5-pyrazolone (*X*)

A suspension of 4-benzyl-3-carbethoxyamino-1-phenyl-5-pyrazolone (2 gm.) in sodium hydroxide was refluxed for two hours. The solution was then cooled and neutralized with acetic acid. A white solid precipitated and was recrystallized from ethanol: m.p. 206° to 207°C. Calc. for $C_{16}H_{15}ON_3$: N, 15.8%. Found: N, 15.5%.

4-Benzyl-3-benzoylamino-1-phenyl-5-pyrazolone

A mixture of 4-benzyl-3-amino-1-phenyl-5-pyrazolone (2 gm.) and benzoyl chloride (2 ml.) in anhydrous dioxane (25 ml.) was heated on a water bath for 18 hr. The solution was evaporated to dryness under reduced pressure to eliminate the benzoyl chloride. The residue was recrystallized twice from ethanol: m.p. 225° to 227°C. Calc. for $C_{23}H_{19}O_2N_3$: N, 11.4%. Found: N, 11.1%.

4-Benzyl-3-benzoylamino-2-phenyl-5-pyrazolone

This 3-benzoylamino derivative was prepared by the method outlined above from 4-benzyl-3-amino-2-phenyl-5-pyrazolone (2). The compound was recrystallized from a large volume of ethanol: m.p. 197° to 198°C. Calc. for $C_{23}H_{19}O_2N_3$: N, 11.4%. Found: N, 11.3%.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra were determined on a Beckman Model DU spectrophotometer, and the experimental details have been reported previously (4). The intensities of the absorption maxima are given in Table II.

The spectra of several 4-monoalkyl-3-amino-5-pyrazolones have been measured and the curves found to agree closely with those of the 4-methyl and 4-ethyl derivatives reported previously (2, 3). In Fig. 1 the spectra of 4-benzyl-3-amino-1-phenyl-5-pyrazolone (X) and the corresponding 2-phenyl derivative (XI) are shown. On acidification of the solution the spectrum of the 1-phenyl derivative is unchanged but that of the 2-phenyl is displaced to longer wave lengths. The spectrum of 4-benzyl-2-phenyl-3-amino-5-pyrazolone resembles those of the 4-methyl-2-phenyl and 4-ethyl-2-phenyl derivatives (2, 3); the spectrum of the 4-acetyl-2-phenyl derivative is alsó similar (Fig. 2).

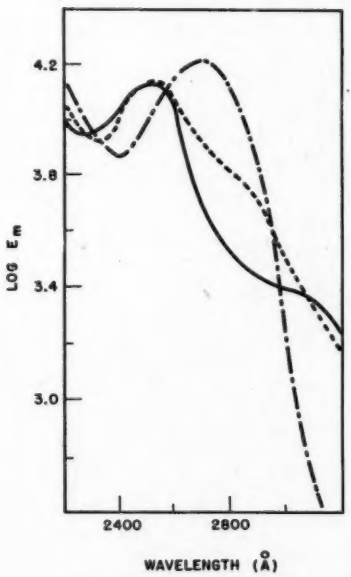


Fig. 1. ———— *4-Benzyl-3-amino-1-phenyl-5-pyrazolone (neutral).*
— — — — *4-Benzyl-3-amino-2-phenyl-5-pyrazolone (neutral).*
— - — - — *4-Benzyl-3-amino-2-phenyl-5-pyrazolone (acid).*

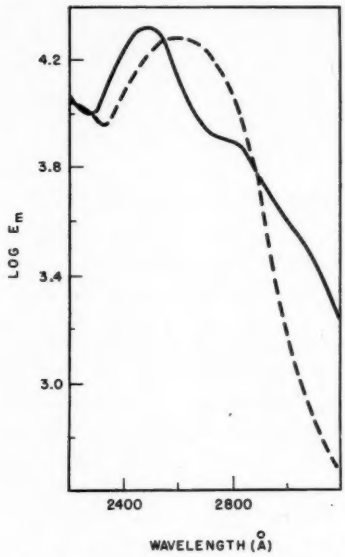


FIG. 2. ———— *4-Acetyl-3-amino-2-phenyl-5-pyrazolone (neutral).*
— — — — *4-Acetyl-3-amino-2-phenyl-5-pyrazolone (acid).*

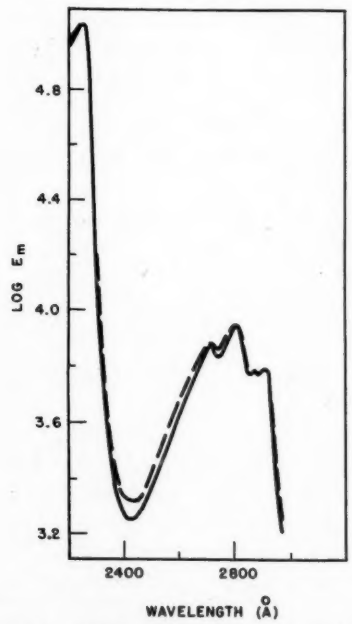
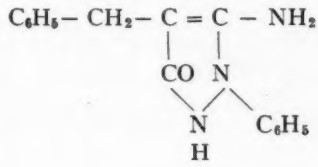


FIG. 3. ———— *4-(α-Naphthyl)-3-amino-2-carboxamido-5-pyrazolone (neutral).*
— — — — *4-(α-Naphthyl)-3-amino-2-carboxamido-5-pyrazolone (acid).*



XI

Several carboxamide and carboethoxy pyrazolones have also been examined. The curve for 4-(α-naphthyl)-3-amino-2-carboxamido-5-pyrazolone shown in Fig. 3 is dominated by the naphthalene chromophore. The 3-imido-2-carboxamido-5-pyrazolones disubstituted at position 4 give absorption curves which are all very similar (Table II and Fig. 4). In the case of the 4, 4-diamyl derivative, measurements have been made also in alkaline solution and maxima observed at 2520 Å (log E_m = 4.19) and 2950 Å (log E_m = 3.70).

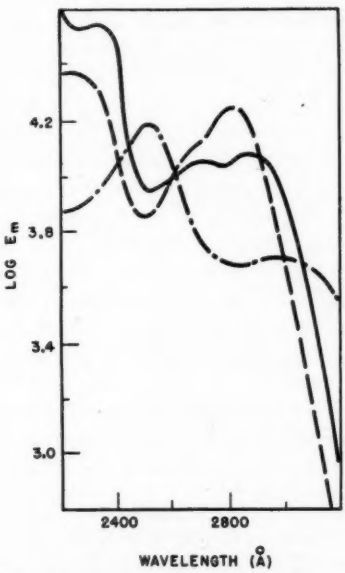


FIG. 4. ———— *4, 4-Diamyl-3-imino-2-carboxamido-5-pyrazolone (neutral).*
— — — — *4, 4-Diamyl-3-imino-2-carboxamido-5-pyrazolone (acid).*
—·—·— *4, 4,-Diamyl-3-imino-2-carboxamido-5-pyrazolone (alkaline).*

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C^{13} ISOTOPE EFFECT IN THE DECARBOXYLATION OF NORMAL MALONIC ACID[1]

By J. G. Lindsay,[2] A. N. Bourns, and H. G. Thode

Abstract

An investigation has been made of the relative rates of decarboxylation of two isotopic species of malonic acid, one containing only C^{12} carbon atoms and the other containing a C^{13} in a carboxyl position. Two effects were observed using malonic acid containing a normal abundance of C^{13}—(1) a 3.3% faster rate of reaction for the molecule containing only C^{12} carbon atoms; (2) a 2% greater probability of rupture of a C^{12}–C^{12} bond than a C^{12}–C^{13} bond in the molecule containing a C^{13} carbon. The latter effect was found to be independent of temperature. The magnitude of the isotope effect is in reasonable agreement with theoretical predictions.

Introduction

Until recently isotope effects in nonequilibrium processes were believed to be negligible except in those cases where deuterium was involved. During the past two years, however, isotope effects in unidirectional processes have been reported for compounds containing isotopic atoms other than deuterium, namely, C^{13}, C^{14}, and N^{15}. Stevenson, *et al.* (1), while investigating propane-1-C^{13} in a mass spectrometer, found that the probability of rupture of C^{12}–C^{13} and C^{12}–C^{12} bonds differed by about 20%. In the thermal cracking of propane-1-C^{13} the effect was smaller, an 8% more frequent rupture of C^{12}–C^{12} than of C^{12}–C^{13} bonds being observed (13). More recently, Yankwich and Calvin (15) found that the specific activity of the CO_2 produced from the decomposition of malonic acid containing C^{14} in a carboxyl group was significantly less than that calculated on the basis of equal probabilities of rupture of C^{12}–C^{12} and C^{12}–C^{14} bonds. Bigeleisen and Friedman (4) have reported a much smaller effect with C^{13} using normal malonic acid. Isotope effects of a similar nature have also been observed in the decomposition of normal oxalic acid (9) and in the hydrolysis of C^{14} labeled esters (12). In this laboratory a 1–2% greater probability of rupture of C^{12}–N^{14} bonds than of C^{12}–N^{15} bonds has been found in the deammonation of phthalamide.*

The case of malonic acid is particularly interesting. Calvin, using C^{14} labeled malonic acid, obtained a 12% isotope effect. Bigeleisen and Friedman, using normal malonic, found a much smaller effect with C^{13} than one would expect from Calvin's results, if the assumption is made that the effect with C^{13} should be one-half that found with C^{14}. A theoretical treatment, based on the postulates of statistical mechanics and the absolute reaction rate theory, (6) has been developed by Bigeleisen (2) to account for these effects. Calculations

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A contribution from the Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ontario.
[2] *Holder of a National Research Council of Canada Studentship.*
* *The results of this investigation are to be reported in a later paper.*

based on this theory agree to some extent with his experimental results, but give values much too small to account for the results reported by Calvin. Pitzer (10), using Bigeleisen's method, but making different approximations, has produced a value which is substantially in agreement with Calvin's experimental results.

The disagreement among the various workers on the magnitude of the effect with malonic acid containing C^{13} and C^{14} atoms, as well as the need for conclusive results to corroborate or disprove any theory advanced to explain these effects, suggests the need for further careful work on this problem. This paper presents the results of an investigation carried out in this laboratory to determine the relative probabilities of rupture of C^{12}–C^{13} bonds as compared to C^{12}–C^{12} bonds in malonic acid containing a normal abundance of C^{13}.

Theory

The thermal decomposition of normal malonic acid may be represented by the following equations:

$$C^{12}H_2(C^{12}OOH)_2 \xrightarrow{k_1} C^{12}O_2 + C^{12}H_3C^{12}OOH \quad (1)$$

$$C^{13}H_2(C^{12}OOH)_2 \xrightarrow{k_2} C^{12}O_2 + C^{13}H_3C^{12}OOH \quad (2)$$

$$C^{13}OOH\,C^{12}H_2\,C^{12}OOH \xrightarrow{k_3} C^{13}O_2 + C^{13}H_3C^{12}OOH \quad (3)$$

$$C^{12}OOH\,C^{12}H_2\,C^{13}OOH \xrightarrow{k_4} C^{12}O_2 + C^{12}H_3C^{13}OOH \quad (3')$$

According to Bigeleisen's calculations (2), the approximate ratio of the rate constants $\frac{k_1}{2k_3}$ and $\frac{k_1}{2k_4}$ is given by

$$\frac{k_1}{2k_3} = \left(\frac{m_3^*}{m_1^*}\right)^{\frac{1}{2}}\left[1 + \sum_i^{3n-6} G(u_i)\Delta u_i - \sum_i^{3n-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}\right] \quad (4)$$

and

$$\frac{k_1}{2k_4} = \left(\frac{m_4^*}{m_1^*}\right)^{\frac{1}{2}}\left[1 + \sum_i^{3n-6} G(u_i)\Delta u_i - \sum_i^{3n-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}\right], \quad (5)$$

where m^*'s are the effective masses of the activated complexes along the coordinates of decomposition and are calculated as being the reduced mass across the bond being broken (3), $\Delta u_i = \frac{hc}{kT}(\omega_{1_i} - \omega_{2_i})$, where the ω's are the vibrational frequencies in cm.$^{-1}$, $G(u_i)$ is a function defined by Bigeleisen and Mayer (5) and ‡ refers to the activated complex.

The ratio $\frac{k_4}{k_3}$, which determines the relative rates of rupture of C^{12}–C^{12} and C^{12}–C^{13} bonds, is then given by

$$\frac{k_4}{k_3} = \left(\frac{m_3^*}{m_1^*}\right)^{\frac{1}{2}} \Big/ \left(\frac{m_4^*}{m_1^*}\right)^{\frac{1}{2}} = \left(\frac{m_3^*}{m_4^*}\right)^{\frac{1}{2}} **.$$

It is seen that this ratio is independent of temperature and depends only on the reduced mass across the bonds being broken. The ratios $\frac{k_1}{2k_3}$ and $\frac{k_1}{2k_4}$, however, are functions of temperature and should decrease with increasing temperature, $\frac{k_1}{2k_3}$ decreasing to the value $\frac{m_3^*}{m_1^*}$ and $\frac{k_1}{2k_4}$ decreasing to unity, since $m_4^* = m_1^*$.

Calculations

The decomposition of malonic acid has been shown to be of first order (7, 8). Therefore, at any time t

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_3 M_3^0 (1 - e^{-(k_3+k_4)})}{(k_3 + k_4)\left[M_1^0(1 - e^{-k_1 t}) + M_2^0(1 - e^{-k_2 t}) + \frac{k_4}{k_3 + k_4} M_3^0\left(1 - e^{-(k_3+k_4)t}\right)\right]}, \quad (6)$$

where M_1^0, M_2^0, and M_3^0 are the initial amounts of the different isotopic species of malonic acid in Equations (1), (2), (3) and (3′) respectively.

When $t = \infty$, Equation (6) becomes

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_3 M_3^0}{(k_3 + k_4)\left[M_1^0 + M_2^0 + \frac{k_4}{k_3 + k_4} M_3^0\right]}, \quad (7)$$

and when t is small (6) becomes

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_3 M_3^0}{k_1 M_1^0 + k_2 M_2^0 + k_4 M_3^0}. \quad (8)$$

Let a be the atom fraction of C^{13} occurring in the normal malonic acid used. If we assume that the ratio of the carbon isotopes is the same in the methylene and carboxyl positions (see page 198), we can calculate the mole fraction of the three isotopic species of malonic acid in terms of a, i.e.,

$$M_1^0 = (1 - 3a)$$
$$M_2^0 = a$$
$$M_3^0 = 2a.$$

** *Dr. Bigeleisen has pointed out that this is an approximation, the correct value being* $\frac{k_4}{k_3} = \left(\frac{m_3^*}{m_4^*}\right)^{\frac{1}{2}}[1 - \Sigma_i G(u_i^{\ddagger})(u_{4i} - u_{3i})]$. *The term in square brackets, however, is negligible (cf. J. Chem. Phys. 18: 1325. 1950.)*

Substituting these values in Equations (7) and (8) and making the approximations $k_4 \approx k_3 \approx \frac{k_1}{2}$; $k_1 \approx k_2$ in the denominator we obtain:

At $t = \infty$

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{2k_3a}{(k_3 + k_4)(1 - a)}, \tag{9}$$

or rearranging

$$\frac{k_4}{k_3} = \frac{2a}{1 - a}\left[\frac{C^{12}O_2}{C^{13}O_2}\right] - 1. \tag{9'}$$

At t small

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{2k_3a}{k_1(1 - a)}, \tag{10}$$

or

$$\frac{k_1}{2k_3} = \frac{a}{1 - a}\left[\frac{C^{12}O_2}{C^{13}O_2}\right]. \tag{10'}$$

If the thermal decarboxylation of malonic acid is taken to completion, a mass spectrometric analysis of the CO_2 produced gives the values of $\frac{C^{12}O_2}{C^{13}O_2}$ in Equation (9'). The ratio $\frac{a}{1 - a}$ is obtained directly from the $\frac{C^{13}O_2}{C^{12}O_2}$ ratio in the CO_2 produced when a sample of the malonic acid is completely converted to CO_2. The ratio $\frac{k_4}{k_3}$ may be obtained in this way. The same ratio may also be obtained from a mass spectrometric analysis of the CO_2 formed on complete oxidation of the acetic acid produced. The equation obtained for the CO_2 of acetic acid oxidation is

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{\frac{2k_4a}{k_3 + k_4} + a}{2(1 - 3a) + \frac{2k_4a}{k_3 + k_4} + \frac{4k_3a}{k_3 + k_4} + a}, \tag{11}$$

or solving for k_4/k_3

$$\frac{k_4}{k_3} = \frac{2 - a\left[1 + \frac{C^{12}O_2}{C^{13}O_2}\right]}{3a\left[1 + \frac{C^{12}O_2}{C^{13}O_2}\right] - 2}. \tag{11'}$$

If the first CO_2 evolved from a decomposition experiment is collected and analyzed mass spectrometrically, the $\frac{C^{12}O_2}{C^{13}O_2}$ ratio obtained may be substituted in Equation (10'), together with the previously determined value for $\frac{a}{1 - a}$, and $\frac{k_1}{2k_3}$ obtained. Combination of the values obtained for $\frac{k_1}{2k_3}$ and

$\frac{k_4}{k_3}$ will give $\frac{k_1}{k_3 + k_4}$, which is a measure of the relative reaction velocities of the two isotopic molecular species M_1^0, and M_3^0.

Experimental

The malonic acid used in the investigation came from two sources. Runs 50–1 to 50–4, including Runs II and *Z*, were made with Eastman Kodak malonic acid. Runs 50–5 to 50–9 involved B.D.H.—C.C. Malonic acid. These chemicals were further purified by recrystallization from water. Three-gram quantities of malonic acid were decomposed in a test tube like reaction vessel, the carbon dioxide and acetic acid produced being swept on by a stream of nitrogen purified by passage through liquid air. The acetic acid was separated in a dry ice–acetone trap and the carbon dioxide collected in barium hydroxide solution as barium carbonate. The reaction vessel was maintained to within ± 0.5°C. of the desired reaction temperature by means of a thermostatically controlled bath.

With the exception of Run *Z*, the oxidation of acetic and malonic acid samples was carried out over hot copper oxide in a quartz combustion tube at 700°–800°C. by a method similar to that described by Rittenberg (11). In Run *Z* the malonic and acetic acids were oxidized using a wet oxidation procedure (14). The carbon dioxide formed was collected and purified in a high vacuum system.

In order to test the validity of the assumption that the ratio of the carbon isotopes is the same in the methylene and carboxyl positions, the methylene carbon atom was converted to carbon dioxide and its $C^{12}O_2/C^{13}O_2$ ratio compared with the average ratio for the three carbon atoms as determined from the carbon dioxide obtained by oxidation of malonic acid. This was done stepwise using Eastman Kodak malonic acid. Acetic acid from a decarboxylation experiment was converted to sodium acetate by means of sodium carbonate. The sodium acetate was heated with soda lime in a stream of pure nitrogen to produce methane of methyl origin. The decomposition products were passed through potassium hydroxide and sulphuric acid bubblers to remove carbon dioxide and any unsaturated hydrocarbon. The methane and nitrogen continued over copper oxide maintained at 750°C. in a quartz tube whereby the methane was oxidized to carbon dioxide and collected as barium carbonate in barium hydroxide solution.

The barium carbonate samples were converted into carbon dioxide for mass spectrometric analysis by acidification with phosphoric acid using standard high vacuum techniques. Experiments in which the decarboxylation reaction was carried to completion were conducted at 138°C. and, where possible, both the carbon dioxide and acetic acid were used in determining the k_4/k_3 ratio. In addition, four decarboxylation reactions were taken to completion at higher temperatures in order to investigate a possible temperature effect. In these experiments the carbon dioxide only was collected.

As an additional experiment, 100 gm. of malonic acid was decarboxylated at 138°C. and the carbon dioxide sample, formed by the decomposition of the first 1% of the acid, was collected separately as barium carbonate. The results of this experiment permit the calculation of the $k_1/2k_3$ ratio. Combination of this ratio with the previously determined value of the ratio k_4/k_3 gives a value of $\frac{k_1}{k_3 + k_4}$.

Mass Spectrometer Analysis

All carbon dioxide samples were analyzed in a 180° direction focusing mass spectrometer. The ion currents were amplified by a total feedback d-c. amplifier using an 954 electrometer tube in the first stage of amplification. The output was fed into a Leeds and Northrup Speedomax recorder. The $C^{12}O_2/C^{13}O_2$ ratio was obtained from the ratio of mass 44/mass 45 ion currents after applying a suitable correction for the contribution to mass 45 of the molecular species $C^{12}O^{16}O^{17}$. Each CO_2 sample was measured relative to a standard, the standard being a CO_2 sample from a malonic acid oxidation. The absolute C^{12}/C^{13} ratio of the standard varied somewhat from day to day but, since all samples were analyzed relative to that standard, it was assigned a C^{12}/C^{13} ratio of 92.77 and the ratios obtained for the various samples corrected relative to this value. The procedure was to analyze the standard, the sample, and the standard again as rapidly as possible. The analysis was considered satisfactory only if the two standards checked to within 0.1%, the precision of a single analysis. Automatic magnetic scanning was used throughout. A single analysis consisted of six or seven spectrograms, each spectrogram consisting of masses 44 and 45 and then by reversing the direction of scan, masses 45 and 44.

Results and Discussion

In general, the k_4/k_3 ratios calculated on the basis of the acetic acid results are lower than those obtained from the decarboxylation of carbon dioxide. The over-all average value for k_4/k_3, using Eastman Kodak malonic acid, is 1.026 ± 0.002 (cf. Table I).

Using B.D.H. malonic acid the average value obtained at four different temperatures is 1.021 ± 0.002 (Table II), a value in excellent agreement with that found by Bigeleisen and Friedman (4) at 138°C. The magnitude of k_4/k_3 and its temperature independence lends good support to Bigeleisen's calculations as well as to the method of calculating the m^*'s.

The assumption that the methylene carbon had a normal $C^{12}O_2/C^{13}O_2$ ratio appears valid in light of the results in Table III for the E.K. acid. One possible explanation for the lack of agreement between the k_4/k_3 values from E.K. and B.D.H. malonic acid would be that while the E.K. acid was synthesized with no fractionation of C^{13} in the methylene position the B.D.H. chemical had undergone fractionation. If the methylene carbon of B.D.H. malonic acid were

TABLE I

INTRAMOLECULAR ISOTOPE EFFECT IN NORMAL MALONIC ACID*

Run	$\frac{C^{12}O_2}{C^{13}O_2}$ **		k_4/k_3	
	CO_2 (Decarboxylation)	Acetic acid	CO_2	Acetic acid
50–1	93.96	–	1.026	
50–2	93.87	–	1.024	
50–3	94.22	92.33	1.031	1.019
50–4	94.43	92.24	1.036	1.023
II	–	92.22	–	1.024
Z–3***	93.88	92.06	1.024	1.031
Mean			1.028 1.026 ± 0.002	1.024

* *Eastman Kodak malonic acid, runs at 138° ± 0.5°C.*

** *All $C^{12}O_2/C^{13}O_2$ ratios are relative to the $C^{12}O_2/C^{13}O_2$ in a normal malonic acid combustion sample arbitrarily chosen as 92.77, i.e.,* $\frac{(1-a)}{a} = 92.77$.

*** *Acetic and malonic acid samples oxidized by sulphuric acid–phosphoric acid solution.*

TABLE II

INFLUENCE OF TEMPERATURE ON INTRAMOLECULAR EFFECT*

Run	Temperature, °C.	$\frac{C^{12}O_2}{C^{13}O_2}$**	k_4/k_3
50–5	138° ± 0.5	93.70	1.020
50–6	151° ± 0.5	93.70	1.020
50–8	174° ± 0.5	93.88	1.024
50–9	199° ± 0.5	93.74	1.021
Mean			1.021 ± 0.001

* *B.D.H malonic acid.*

** *All $C^{12}O_2/C^{13}O_2$ ratios are relative to the $C^{12}O_2/C^{13}O_2$ in a normal malonic acid combustion sample arbitrarily chosen as 92.77, i.e., $(1-a)/a = 92.77$.*

TABLE III

$\frac{C^{12}O_2}{C^{13}O_2}$ RATIO OF METHYLENE CARBON IN E.K. MALONIC ACID*

Run	$\frac{C^{12}O_2}{C^{13}O_2}$**	
	CO_2 from malonic acid oxidation	CO_2 from methylene carbon
I	92.77	92.79
II	92.77	92.80

**Temperature 138°C.*

***$C^{12}O_2/C^{13}O_2$ ratios are relative to the $C^{12}O_2/C^{13}O_2$ in an normal malonic acid combustion sample arbitrarily chosen as 92.77, i.e.,* $\frac{(1-a)}{a} = 92.77$.

0.5% less abundant in C^{13} than the average for the three carbon atoms, the results with E.K. and B.D.H. would be consistent.

The value for $\frac{k_1}{k_3 + k_4}$ at 138°C. found with Eastman Kodak acid is somewhat larger than that found by Bigeleisen and Friedman (4). It follows from Bigeleisen's calculations that this effect should decrease to a constant value as the temperature is increased. This was not checked. It is of interest to note in Table IV that there has been a 12% change effected in the ratio of the carbon isotopes between the first and last CO_2 fraction.

Table V compares the results obtained in the present investigation with those of Bigeleisen and Friedman. The agreement is good and lends excellent support to the theory as far as k_4/k_3 is concerned. The disagreement of $k_1/2k_3$ with theory indicates that the model used in calculations of the vibrational frequencies was oversimplified and, as Bigeleisen and Friedman have pointed out, the calculations should be more consistent with experimental results when the vibrational frequencies of malonic acid are known.

TABLE IV

INTERMOLECULAR ISOTOPE EFFECT IN NORMAL MALONIC ACID*

Sample	$\frac{C^{12}O_2}{C^{13}O_2}$	$\frac{k_1}{2k_3}$	$\frac{k_1}{k_3 + k_4}$ **
1st CO_2 evolved	97.05	1.046	1.033
Last CO_2 evolved	86.83		

E.K. malonic acid; run at 138° ± 0.5°C.
$\frac{C^{12}O_2}{C^{13}O_2}$ ratios are relative to malonic acid standard as 92.77.
***Assuming $k_4/k_3 = 1.026$.*

TABLE V

COMPARISON OF RESULTS

	Bigeleisen & Friedman	Present work		Theory (Bigeleisen)
		B.D.H. Mal.	E.K. Mal.	
$\frac{k_1}{2k_3}$	1.037	–	1.046	1.021
$\frac{k_4}{k_3}$	1.020	1.021	1.026	1.020

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THE AGING OF AMMONIUM CHLORIDE SMOKES[1]

By T. Gillespie and G. O. Langstroth

Abstract

In an extension of earlier work, studies have been made of the time variations in the particle number and size and mass concentration of 'still' ammonium chloride smokes having a wide range of initial mass concentration. Direct measurement of losses to chamber surfaces was an important feature of the experiments since it provided an additional quantity to be satified by theory and permitted a more critical evaluation of the coagulation and loss constants than was previously possible. Satisfactory agreement was found between theory and observation. The dependence of the loss constant on smoke chamber dimensions was found to be in accordance with expectation. The coagulation constant was 4.3×10^{-8} cc. per min. for the least dense, but tended to a larger value for the more dense smokes. A revision of the constants obtained from earlier data indicated that the coagulation constant was little affected by turbulent air motion below a more or less critical value.

It has been shown previously (2) that time variations in the particle number of ammonium chloride smokes in still and moving air are described by equations deduced on the assumption that the rates of coagulation and loss to surfaces are proportional respectively to the square and to the first power of the particle number. Application of the equations to the data permitted evaluation of the loss and coagulation constants. The experiments, however, were limited to an approximately constant initial mass concentration of smoke (40 mgm. per m.^{3}). Furthermore, as was pointed out, the procedure employed in the analysis of data did not lead to a very critical evaluation of the constants for still or slightly moving air, although it was satisfactory for the data obtained with the more rapid air motions.

New experiments have been performed with ammonium chloride smoke in 'still' air over a wide range of initial mass concentration (36 to 420 mgm. per m.^{3}). In many of them the rate of loss of particles to surfaces was determined directly in addition to measurements of particle number and size and mass concentration. These determinations were an important feature since (*a*) they provided data for an additional quantity to be satisfied by theory, and (*b*) they permitted use of a more critical procedure for calculation of the coagulation and loss constants. A special set of experiments was performed with a series of chambers of graded size ranging from 11.8 to 0.0033 m.^{3} in order to test the predicted dependence of the loss constant on the ratio of the wall surface area to the chamber volume.

All the data, including those for the rate of particle loss to surfaces and its dependence on chamber size, were in accord with the theory. In the light of the newer results some revision was desirable in the constants for 'still' and slightly moving air as deduced from earlier data (2). On the basis of this revision it appears that the coagulation constant is little affected by turbulent air motion

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when the average rate of flow through a given small volume is less than 40 m. per min. The increased rate of disappearance of smoke with stirring under these conditions is attributed predominantly to an increased loss rate by impingement of particles on surfaces.

1. Apparatus and Procedure

Three different approximately cubical smoke chambers having volumes of 11.8 m.^{3}, 0.22 m.^{3}, and 0.0033 m.^{3} were used in the experiments. In general the smoke was produced by an external generator in the manner previously described (2), but in some experiments it was formed inside the large chamber by placing a Petrie dish containing a weighed amount of ammonium chloride on a hot plate before a fan. Smoke for the smallest chamber was obtained during the generation of a cloud in the 0.22 m.^{3} chamber. With few exceptions (e.g., Expt. S.B. 10) the reproducibility of smoke production was comparable to that previously reported (2), regardless of the method used; initial particulate numbers and mass concentration varied from the mean for similar conditions by less than 30% and 15% respectively.

Particle number, mass concentration, and surface loss samples were taken periodically over an interval of 4.5 hr. in each experiment. The total volume of smoke drawn from any chamber in flushing and sampling during an experiment did not exceed 2% of the chamber volume. Time was reckoned from a zero at the moment of turning off the mixing fan, i.e., three minutes after generation of smoke was complete.

Particle number was assessed from thermal precipitator deposits in the manner previously described (2). Because of the large value under some conditions, it was desirable to dilute the smoke from the chamber before sampling with the precipitator. A suitable technique was found after considerable study. It involved drawing 170 cc. of smoke from the chamber through a 2.5 cm. diameter valve into a brass vessel containing air by lowering the level of oil in the latter. The smoke and air were mixed by four strokes of a vertical stirrer, and 170 cc. of the mixture was flushed through a short 2.5 diameter tube leading to the precipitator. The mixture was then sampled. The validity of the method was established from the concordance of data for samples taken alternately by direct and dilution methods. The dilution factor was 11.4: 1. The technique was used only for smoke of very large particulate number. It was not used in experiments with the smallest chamber; in these the precipitator was mounted directly on the outside of the box to eliminate the necessity of wasteful flushing.

The electrical precipitators and the technique of obtaining samples with them have been described previously (2). Each deposit was dissolved in 50 cc. of distilled water, and the mass concentration was found from electrical conductivity measurements at 25 $\pm$ 0.05°C. with the aid of a calibration curve prepared with known solutions. The conductivity cell had 3.6 cm.^{2} plates 1.5 cm. apart and held 40 cc. of solution; the applied voltage was 110 volts a.c.

By using freshly boiled distilled water for the solutions the mass of the deposit was determinable with an error of less than 5% over the range 0.1 to 1.5 mgm. The conductivity was directly proportional to the mass.

Direct determinations of the number of particles lost to the chamber surfaces during successive periods throughout an experiment were based on assessment of the number of particles deposited on 19 mm. diameter glass slides placed face up on the bottom of the chamber, face down on the top, and vertically at the midpoint of each side wall. The slides were held flush with the surface on brass or plastic plugs which permitted removal and replacement with a fresh slide at selected times. The intervals between replacements were sufficiently short to avoid deposits characterized by appreciable superposition of particles (1). The technique of counting the particles in each deposit was similar to that used for thermal precipitator slides. The number of particles lost to each surface during each successive period in the life of the smoke was estimated from these counts on multiplying by the ratio of the total area of the surface to the area scanned on the slide.

The procedure used in making the estimates described above involved the assumption that losses were uniform over the area of each chamber surface. A series of subsidiary experiments in which smoke in the 11.8 $m.^3$ chamber was sampled simultaneously at different heights and positions by four thermal precipitators of known characteristics was performed to test this point and for reasons to appear later. The disturbance created by sampling was negligible because of the low sampling rate (3 cc. per min.). No differences were found in the particulate numbers at different heights and positions either in the early or late stages of a smoke. The uniform distribution presumably resulted from the occurrence of convection currents; convective motion of particles was apparent on shining a narrow beam of light into the smoke and examination with a long-focus microscope. Since a uniform distribution of smoke must be accompanied by uniformity in the loss rate over each surface, the results support the assumption made. The necessity of mounting slides flush with a flat surface may be noted also since convective air motion can lead to curious patterns about small obstacles.

Particle size distributions were estimated both for thermal precipitator and for surface loss samples with the aid of a Patterson–Cawood graticule, using substage illumination at a magnification of 950 ×. The former refer to air-borne particles and the latter to particles being lost to surfaces.

2. Experimental Data

The time variation of particulate number is illustrated in Fig. 1. Typical surface loss data are shown in Fig. 2. Each point represents a cumulative loss up to the corresponding time and was obtained by adding together the determined losses for all intervals from the beginning of the experiment. The apparent size distributions of air-borne particles and those being lost to surfaces are compared in Fig. 3 for an early and a late stage in the life of a smoke.

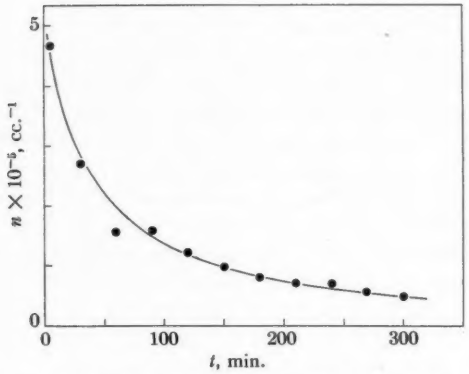

FIG. 1. *Typical particulate number data (Expt. S 29).*

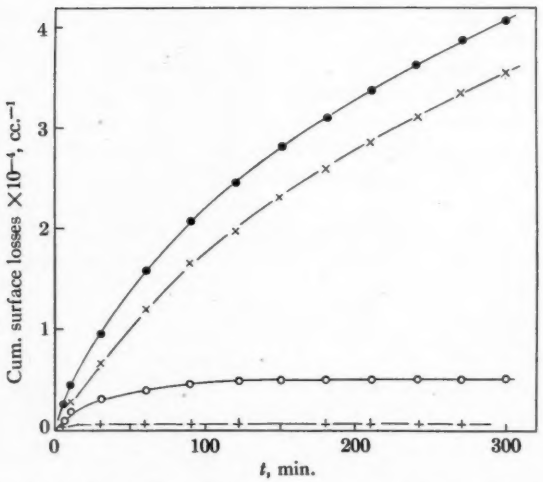

FIG. 2. *Typical surface loss data (Expt. S 29). The plotted points represent the cumulative number of particles lost from the beginning of the experiment to the top (+), side walls (o), and bottom (×) of the chamber, divided by the chamber volume; the sum of the values for all surfaces is indicated by •.*

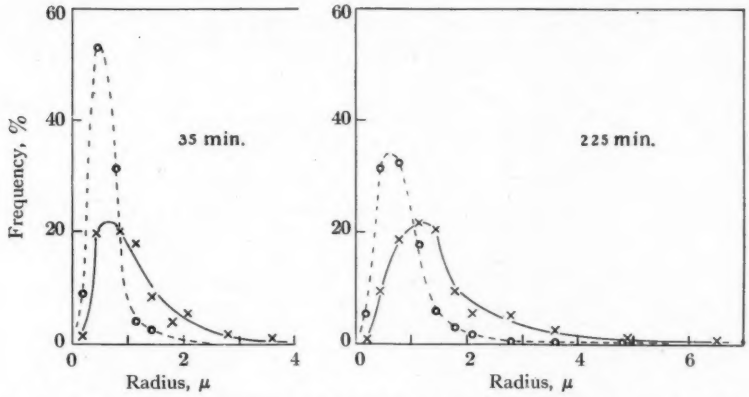

FIG. 3. *Typical size distributions of airborne particles (o) and particles lost to surfaces (×) at early and late stages in an experiment (Expt. S 39). Ordinates represent the per cent frequency of occurrence and abscissas the apparent radii in microns. Each point is plotted at the radius corresponding to the center of its size group.*

Particulate volume and surface loss data for experiments with the 11.8 m.³ chamber (Table I*a*), the 0.22 m.³ chamber (Table I*b*), and the 0.0033 m.³ chamber (Table I*c*), are given in some detail since the method of interpretation differs materially from that used in the past by other workers. Particulate volume data for some experiments in which surface loss was not measured are given in Table II. In these tables, values calculated by the methods of Section 3 are included for comparison with the observed values. Mass concentration data for some of the experiments of Tables I and II are given in Table III.

3. Analysis of the Data

On rather general grounds one may expect (2) that the number of particles per cc. and the mass concentration of a smoke decrease in a time t from initial values of n_0 and m_0 to values given by

$$\ln\left(\frac{1}{n} + \frac{k}{\beta}\right) = \beta t + \ln\left(\frac{1}{n_0} + \frac{k}{\beta}\right), \tag{1}$$

$$\ln(m) = \ln m_0 - \alpha t, \tag{2}$$

where k denotes the coagulation constant, and β and α are constants descriptive respectively of the rate of loss of particles and of mass to adjacent surfaces.

An expression may be obtained easily for the surface loss from systems in which the space distribution of smoke is essentially uniform, as in our experiments (see Section 1). In accordance with the previous treatment (2), the rate of loss of particles to surfaces is taken to be proportional to the number present, i.e.,

$$(dn/dt)_l = -\beta n. \tag{3}$$

TABLE I(*a*)

EXPERIMENTAL DATA OBTAINED IN AN 11.8 M.³ CHAMBER AND A COMPARISON WITH CALCULATED VALUES*

Time (min.)	S 39: M^{**} = 1.02 gm./m.³				S 40: M = 1.02 gm./m.³				S 27: M = 0.5 gm./m.³			
	$10^6/n$		$(\Delta n)_l \times 10^{-3}$		$10^6/n$		$(\Delta n)_l \times 10^{-3}$		$10^6/n$		$(\Delta n)_l \times 10^{-3}$	
	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	1.6	1.5	4.3	2.0	1.8	1.7	3.6	2.5	1.9	1.8	2.8	3.4
10	1.8	1.7	8.0	4.8	–	2.0	6.6	5.5	–	–	–	–
30	3.0	2.7	16.2	15.0	3.4	3.2	13.8	16.0	3.5	3.1	13.0	11.5
60	3.8	4.2	24.1	24.8	5.1	5.0	20.5	23.0	4.4	4.8	19.1	18.6
90	5.5	5.8	30.5	33.8	6.5	6.5	26.0	28.3	7.3	6.5	23.5	23.9
120	7.3	7.5	36.6	38.3	7.1	7.0	30.5	28.2	9.1	8.4	27.2	27.5
150	8.8	9.2	41.6	42.2	8.6	10.2	35.5	36.8	10.5	10.2	30.7	30.4
180	10.5	11.0	46.4	46.0	16.8	13.0	39.5	40.5	11.8	12.1	33.9	32.8
210	13.0	13.0	50.3	50.5	14.0	14.0	42.8	41.0	15.3	14.2	36.5	35.8
240	15.7	14.6	53.6	52.4	17.2	16.2	46.0	44.4	20.8	16.2	38.9	37.5
270	17.0	16.7	56.0	54.0	–	–	–	–	18.8	18.4	41.4	39.4

* *From Equations 1 and 4 with constants as given in Table IV.*
** *M denotes the mass of ammonium chloride dispersed per cubic meter.*

TABLE I(*a*) (*Continued*)

EXPERIMENTAL DATA OBTAINED IN AN 11.8 M.³ CHAMBER AND A COMPARISON WITH CALCULATED VALUES*

Time (min.)	S 29: M^{**} = 0.5 gm./m.³				S 30: M = 0.085 gm./m.³				S 34: M = 0.085 gm./m.³			
	$10^6/n$		$(\Delta n)_l \times 10^{-3}$		$10^6/n$		$(\Delta n)_l \times 10^{-3}$		$10^6/n$		$(\Delta n)_l \times 10^{-3}$	
	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	2.4	2.4	2.4	2.8	2.0	2.0	1.4	1.4	1.6	1.6	1.3	1.3
30	3.8	3.7	9.6	10.8	3.1	3.1	4.3	4.3	3.1	2.6	5.6	5.0
60	6.5	5.2	15.6	16.5	4.4	4.4	6.8	7.5	4.3	3.9	8.6	10.0
90	6.4	6.9	20.8	20.5	5.1	6.0	9.0	10.6	5.5	5.0	11.4	12.9
120	8.1	8.3	24.5	24.3	6.9	7.5	11.2	12.6	6.0	6.3	14.1	15.5
150	10.4	10.1	28.1	27.5	10.6	8.0	13.6	13.4	7.7	7.5	16.7	17.7
180	13.0	12.0	31.1	32.0	9.0	10.0	15.4	15.0	8.1	8.6	19.1	18.4
210	14.3	13.6	33.8	32.3	11.0	12.0	17.0	16.8	10.9	9.9	21.0	20.5
240	14.5	15.5	36.3	34.0	14.9	14.0	18.6	18.3	11.0	11.0	22.0	21.5
270	18.9	17.4	38.7	36.0	16.8	15.0	19.9	18.7	12.8	12.4	24.7	22.7

* *From Equations 1 and 4 with constants as given in Table IV.*
** *M denotes the mass of ammonium chloride dispersed per cubic meter.*

TABLE I(*b*)

EXPERIMENTAL DATA OBTAINED IN A 0.22 M.³ CHAMBER AND COMPARISON WITH CALCULATED VALUES

Time (min.)	R 1 : M = 1.02 gm./m.³				R 2 : M = 1.02 gm./m.³				R 3 : M = 0.085 gm./m.³			
	$10^6/n$		$(\Delta n)_l \times 10^{-3}$		$10^6/n$		$(\Delta n)_l \times 10^{-3}$		$10^6/n$		$(\Delta n)_l \times 10^{-3}$	
	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	Calc.))	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	2.0	2.2	12.8	15.0	1.3	1.2	14.9	14.0	2.4	2.6	3.3	3.1
25	3.9	3.5	45.1	44.0	2.0	2.2	46.9	44.0	3.4	3.5	10.3	10.0
55	6.0	5.7	72.0	75.0	3.7	3.9	74.8	78.0	5.0	4.8	17.4	19.0
85	7.1	8.2	81.7	94.0	6.1	5.9	95.5	100	5.9	6.3	23.9	24.5
115	12.3	11.2	108	107	8.1	8.0	112	113	8.2	7.8	29.5	31.5
145	16.1	14.3	123	119	9.9	10.3	126	124	9.1	9.4	35.2	36.8
175	19.6	18.1	132	126	12.9	12.9	138	132	11.1	11.1	41.3	39.6
205	22.7	21.4	141	131	22.8	15.6	148	135	13.0	12.7	43.8	42.0
235	25.6	27.0	146	140	21.3	18.9	157	140	14.3	14.4	47.1	45.5

See footnote to Table I(a).

TABLE I(*c*)

EXPERIMENTAL DATA OBTAINED IN A 0.0033 M.³ CHAMBER AND COMPARISON WITH CALCULATED VALUES

Time (min.)	SB 6 : M = 1.02 gm./m.³				SB 7 : M = 1.02 gm./m.³				SB 10 : M = 0.085 gm./m.³				SB 11 : M = 0.085 gm./m.³			
	$10^6/n$		$(\Delta n)_l \times 10^{-4}$		$10^6/n$		$(\Delta n)_l \times 10^{-4}$		$10^6/n$		$(\Delta n)_l \times 10^{-4}$		$10^6/n$		$(\Delta n)_l \times 10^{-4}$	
	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	1.6	1.7	2.8	2.7	1.9	1.9	2.5	2.5	–	–	–	–	3.0	2.9	1.9	1.8
7	–	–	–	–	–	–	–	–	3.0	2.9	2.1	2.6	–	–	–	–
20	3.0	2.9	8.0	9.2	3.7	3.3	8.2	7.8	3.7	3.9	5.2	5.6	4.5	4.0	5.1	5.1
47	5.0	5.2	15.3	15.5	7.3	6.4	14.3	14.8	4.9	6.0	9.2	9.8	5.5	6.5	9.5	10.0
75	9.4	8.4	20.6	19.3	11.2	10.4	18.4	17.8	9.2	9.0	12.0	12.8	9.9	9.9	12.9	12.9
105	13.0	12.7	24.0	22.5	14.5	15.9	21.6	21.2	16.1	12.9	13.7	15.2	14.5	14.7	15.4	15.4
135	16.7	18.6	26.9	24.7	25.0	23.4	23.7	22.6	14.1	17.4	15.2	16.1	16.4	21.1	16.9	16.8
165	27.0	26.4	28.8	25.8	35.3	33.7	25.1	24.2	22.0	23.5	16.6	17.7	22.8	29.5	17.5	18.5
190	29.4	34.4	29.6	26.3	39.0	44.4	25.8	25.5	33.3	29.5	17.8	18.8	47.6	38.3	19.0	18.8

See footnote to Table I(a).

TABLE II

EXPERIMENTAL DATA OBTAINED IN AN 11.8 M.³ CHAMBER WITHOUT DIRECT MEASUREMENT OF SURFACE LOSSES, AND A COMPARISON WITH CALCULATED VALUES

Time (min.)	Mass dispersed, 1.02 gm./m.³				Mass dispersed, 0.5 gm./m.³				M = 0.67 gm./m.³		M = 0.085 gm./m.³	
	S 4 : $10^6/n$		S 5 : $10^6/n$		S 6 : $10^6/n$		S 8 : $10^6/n$		S 10 : $10^6/n$		S 12 : $10^6/n$	
	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	1.6	2.1	2.1	1.9	2.2	1.8	1.9	1.9	1.8	1.8	2.7	2.7
35	4.7	4.0	3.3	3.9	3.0	3.2	3.2	3.3	3.0	3.0	3.7	4.0
65	3.0	6.1	6.2	5.9	4.5	4.6	5.5	4.9	5.0	4.8	5.1	5.3
95	8.3	8.3	7.7	8.0	6.9	6.4	6.3	6.4	6.2	6.4	7.6	6.0
125	9.3	10.6	8.8	10.1	6.9	8.0	8.5	8.1	7.5	8.1	8.9	8.2
155	14.8	13.1	12.4	12.4	8.4	9.8	–	9.9	11.4	10.0	10.4	9.0
185	20.8	15.7	15.9	14.9	10.0	11.1	11.4	11.3	11.0	12.0	13.9	11.0
215	20.4	18.3	20.0	17.4	13.2	13.1	14.3	13.1	16.2	14.0	11.2	12.0
245	21.0	21.2	20.0	20.0	14.9	15.0	14.3	15.0	17.3	16.0	14.8	14.0
275	25.1	23.9	23.2	22.9	18.4	17.0	18.6	16.9	18.1	18.1	–	–

See footnote to Table I(a).

TABLE III

MASS CONCENTRATION DATA FOR SOME OF THE EXPERIMENTS OF TABLES I AND II
(The tabulated values are m., (mgm./m.^{3}))

Time, (min.)	S 4	S 5	S 6	S 8	S 10	S 12	S 27	S 44
12	425	357	214	240	325	36.5	235	150
42	336	297	196	189	250	30.0	161	125
72	276	248	157	155	202	29.3	160	107
102	278	228	133	137	187	24.6	148	100
132	221	183	108	115	146	23.8	115	88.2
162	165	173	91.4	96	130	21.6	95	74.0
192	147	131	77.1	83	110	19.7	85.3	69.0
222	137	114	67.3	72.4	93.8	18.3	73.1	60.5
252	118	95	58.0	63.0	82.6	18.5	69.0	52.5
282	96	90	50.3	56.0	72.0	15.4	58.0	46.5

The number of particles lost to surfaces during the period from $t = 0$ to t is then given by

$$(\Delta n)_t = \beta \int_0^t n dt \,, \tag{4}$$

provided β remains essentially constant. Since both Equations (3) and (4) refer to the average loss per cubic centimeter of the system, $(\Delta n)_t$ is to be interpreted as the estimated loss for the whole system divided by the volume of the chamber. According to Equation (4) a plot of $(\Delta n)_t$ as determined from surface loss measurements against $\int_0^t n dt$ as found from the appropriate area under the n vs. t curve (Fig. 1) should yield a straight line of slope β. The linear character of the curves actually obtained is illustrated in Fig. 4 by examples for three experiments.

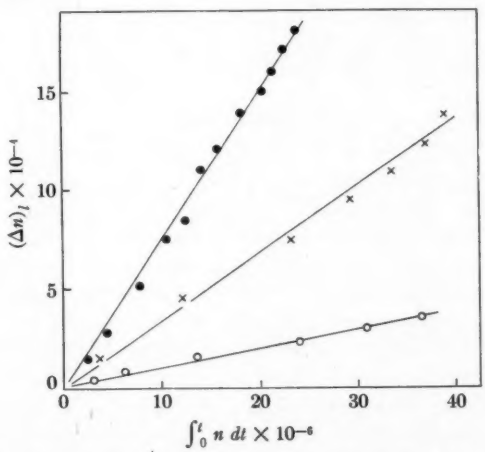

FIG. 4. *Examples of the proportionality between the cumulative surface loss and the area under the particulate number vs. time curve (Expts. SB 10, •; R 2, ×; and S 39, o).*

Values for k and β were found formerly (2) from plots of $\log\left(\frac{1}{n}+E\right)$ vs. t with the constant E selected by trial and error to yield a straight line. This procedure did not permit a very critical evaluation of the constants for 'still' or slightly moving smoke. With the new data a more critical procedure is possible. It follows from Equations (1) and (4) that

$$\ln(n) + \beta t = -\frac{k}{\beta}(\Delta n)_l + \ln(n_0)\,. \tag{5}$$

In accordance with this equation, plots of $\ln(n)+\beta t$, with β found as described above, against $(\Delta n)_l$ yielded straight lines as illustrated in Fig. 5. The value of k was found from the slope of the lines. A few experiments without measurement of surface losses are included in this article; analysis of the data for these was made by the former procedure using an E value consistent with the newer results. Values found for the constants in all experiments are summarized in Table IV.

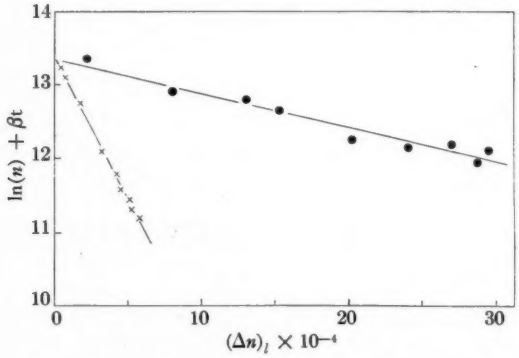

FIG. 5. *Typical* $ln(n)+\beta t$ *vs.* $(\Delta n)_l$ *plots (Expts. S 39,* ×*; and SB 6,* •*).*

4. Discussion

The previous tests (2) of the theory were obtained over a wide range of air motion with smoke of about 40 mgm. per m.^{3} initial mass concentration. It is now apparent from Tables I and II that particulate number data for smokes ranging from 36 to 420 mgm. per m.^{3} initial mass concentration in 'still' air are also adequately described by Equation (1) with experimentally determined values of the constants (Table IV). The average deviation of calculated from observed values was less than 8%. Furthermore, it may be seen from Table I that the cumulative losses of particles to chamber surfaces calculated from Equation (4) using determined β values agree well with observation; the average deviation was less than 6.5%. Two features not previously studied illustrate further the agreement between theory and experiment; (*a*) the direct proportionality between the cumulative surface loss and the area under the particulate number vs. time curve (Fig. 4), and (*b*) the linearity of $\ln(n) + \beta t$

TABLE IV

A SUMMARY OF THE DETERMINED VALUES OF THE CONSTANTS IN THE EXPERIMENTS OF TABLES I AND II

Expt.	M^* (mgm./m³)	m_0^{**} (mgm./m³)	$n_0^{**} \times 10^{-5}$ (cc.$^{-1}$)	$\beta \times 10^3$ min.$^{-1}$	$k \times 10^8$ cc./min.	$k/\beta \times 10^6$	$\alpha \times 10^3$ min.$^{-1}$	α/β	Vol. m.³	$\frac{\text{Surface area}}{\text{Chamber vol.}} \times 10^2$ (cm.$^{-1}$)	$\beta\left(\frac{\text{Chamber vol.}}{\text{Surface area}}\right) \times 10^2$ (cm./min.)
S 12	85	36.0	4.5	0.41	4.1	100	3.0	7.3	11.8	2.62	1.6
S 30	85	–	5.7	0.36	3.9	108	–	–	11.8	2.62	1.4
S 34	85	–	6.7	0.46	3.8	83	–	–	11.8	2.62	1.8
SB 10	85	–	10.9	7.5	5.6	7.5	–	–	.0033	40.5	1.9
SB 11	85	–	3.8	9.0	4.8	5.3	–	–	.0033	40.5	2.2
R 3	85	–	4.4	1.10	3.9	34.8	–	–	.22	10.4	1.1
S 44	250	152	4.2	1.14	5.2	46	4.3	3.8	11.8	2.62	4.4
S 6	500	235	5.8	0.88	4.8	55	5.6	6.4	11.8	2.62	3.4
S 8	500	241	5.3	0.88	4.8	55	5.4	6.1	11.8	2.62	3.4
S 27	500	228	6.9	0.90	5.2	58	4.9	5.5	11.8	2.62	3.4
S 29	500	–	4.8	0.95	4.9	52	–	–	11.8	2.62	3.6
S 10	670	319	8.0	1.23	4.9	40	5.4	4.4	11.8	2.62	4.7
S 4	1020	420	6.2	1.53	6.1	40	5.5	3.6	11.8	2.62	5.8
S 5	1020	375	6.2	1.47	5.9	40	5.4	3.7	11.8	2.62	5.6
S 39	1020	–	8.3	0.99	4.1	40.8	–	–	11.8	2.62	3.8
S 40	1020	–	7.1	1.02	4.8	47.8	–	–	11.8	2.62	3.9
SB 6	1020	–	7.1	9.0	5.1	5.6	–	–	.0033	40.5	2.2
SB 7	1020	–	6.3	8.5	5.6	6.6	–	–	.0033	40.5	2.1
R 1	1020	–	5.6	3.8	5.1	13.3	–	–	.22	10.4	3.7
R 2	1020	–	12.5	3.4	5.1	15.0	–	–	.22	10.4	3.3

* *M signifies the mass dispersed (mgm./m.³).*
** *m_0 and n_0 were obtained by extrapolation of the appropriate time curves.*

vs. $(\Delta n)_l$ plots (Fig. 5). Under all conditions plots of log (m) vs. t for mass concentration data (e.g., those of Table III) yielded straight lines in accordance with Equation (2) and the previous finding (2).

It may be seen from Table IV that the loss constant β for various conditions ranged from 0.36×10^{-3} to 1.35×10^{-3} min.$^{-1}$ with the 11.8 m.^{3} chamber, from 3.4×10^{-3} to 4.4×10^{-3} min.$^{-1}$ with the 0.22 m.^{3} chamber, and from 7.5×10^{-3} to 9.0×10^{-3} min.$^{-1}$ with the 0.0033 m.^{3} chamber. A dependence on chamber dimensions is to be expected since the total rate of loss of particles to surfaces must be proportional to the surface area in contact with the smoke, and also to the product of β and the volume of smoke in accordance with Equation (3). In other words "$\beta \times$ chamber volume/chamber surface area" should be independent of the dimensions of the chamber for smokes having the same characteristics. Some variation in this quantity must be expected for the range of smoke characteristics in our experiments since the loss rate depends on such factors as particle size. Examination of Table IV shows that although the ratio of volume to surface area of the chambers varied by a factor of nearly 16: 1, individual values of the quantity varied by a factor of 2 or less with smokes produced by the dispersal of 85 mgm. per m.^{3} of ammonium chloride, and by a factor of 2.8 or less with those produced by dispersal of 1020 mgm. per m.^{3}

The percentages of the airborne particles and mass lost per minute from the system by impingement on surfaces are given respectively by 100 β and 100 α. These loss rates increased with the initial particle size as shown in Fig. 6. The loss rate of particles of 6×10^{-13} gm. average initial mass, was about 2.5 times greater than that of particles 2×10^{-13} gm. average initial mass, but the mass loss rate was only about 1.4 times greater. The quantity α/β should be equal to the ratio of the average mass of particles lost to surfaces to that of airborne particles (2). Its value lay between 3.6 and 7.3 (Table IV). This is approximately the value estimated from size distribution curves (e.g., Fig. 3), assuming the same density for all particles

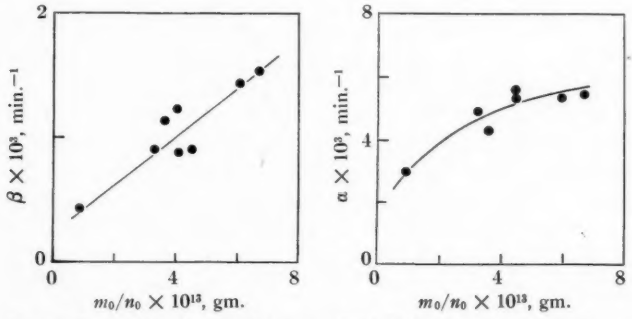

FIG. 6. *The variation of β and α with the average initial particle mass. The data were obtained with the 11.8 m.^{3} chamber.*

Values obtained for the coagulation constant ranged from 3.8×10^{-8} to 6.1×10^{-8} cc. per min. (Table IV), with an average value of 4.3×10^{-8} cc. per min. for the least dense smoke. Since the average for the most dense smoke was 5.2×10^{-8} cc. per min. there appears to be some tendency for this quantity to increase with increased mass concentration and average particle size. No explanation of this tendency can be advanced at the moment in view of our lack of definite information on the part played by the various mechanisms responsible for coagulation.

The value of the coagulation constant is larger than that previously reported (2) for 'still' air. It is considered more reliable since analysis of the previous data was made by a less critical method. In view of the importance of information on the behavior of systems in moving air, it seemed desirable to re-examine the earlier data to see if they could be described using constants consistent with the newer results. It was found that use of the revised constants as given in Table V led to a slightly better agreement between calculated and observed particulate number data (average deviation 6.0% as compared to the former 6.3%).

The dependence of the revised constants on the degree of air motion (V, m. per min.) is shown in Fig. 7. It appears that the rate of loss of particles to

TABLE V

REVISED CONSTANTS FROM PREVIOUS DATA (2) FOR MOVING AIR

Expt.	V, (m./min.)	$\beta \times 10^3$ (min.$^{-1}$)	$k \times 10^8$ cc./min.	$k/\beta \times 10^6$	$\alpha \times 10^3$ (min.$^{-1}$)	α/β
D 38	0.0	1.13	4.5	40	3.2	2.8
D 40	0.0	1.29	5.2	40	3.4	2.6
W 80	0.0	1.15	4.6	40	3.6	3.1
D 75	1.1	1.8	5.1	28	5.2	2.9
D 74	5.4	3.6	5.4	15	6.2	1.7
D 76	11	4.0	5.6	14	8.3	2.1
D 77	11	3.5	4.9	14	7.4	2.1
W 78	11	3.5	4.6	13	6.8	1.9
W 79	11	3.3	4.6	14	6.2	1.9
D 73	22	5.1	5.1	10	9.0	1.8
D 56	29	5.5	3.9	7	8.1	1.5
D 58	29	5.9	4.2	7	8.5	1.4
D 62	35	7.0	4.2	6	9.6	1.4
D 63	35	7.2	4.3	6	9.6	1.3
D 54	40	8.0	4.8	6	10.8	1.4
D 55	40	8.1	4.8	6	11.0	1.4
W 81	40	8.5	4.3	5	10.8	1.3
D 51	50	9.4	6.6	7	14.0	1.5
D 60	50	9.8	6.9	7	12.8	1.3

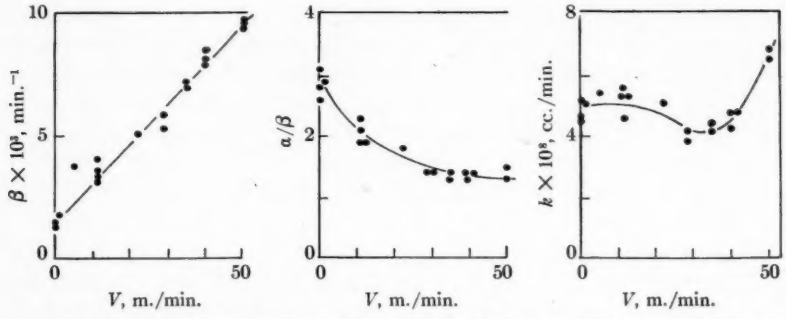

FIG. 7. *Dependence of constants on the degree of turbulent air motion in a 1.12 m.³ chamber (from a re-examination of earlier data).*

surfaces increased approximately linearly with the degree of air motion. Since α/β was greater than unity, loss of the larger particles was favored, but since it decreased with increasing air motion this preference was less marked with rapidly moving air. It is not certain that the dip in the k vs. V curve is real. In any event, the coagulation constant was little affected by changes in the degree of air motion until the V value exceeded 40 m. per min.

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THE ESTIMATION OF SOME 17-ALKYL-SUBSTITUTED STEROIDS WITH THE ZINC CHLORIDE – ACETYL CHLORIDE (TSHUGAEV) REAGENT AND A POSTULATED REACTION MECHANISM[1]

By R. H. Cox[2] and E. Y. Spencer

Abstract

The reactivity of a number of 17-alkyl-substituted steroids toward the zinc chloride – acetyl chloride (Tshugaev) reagent has been investigated. Maximum absorption values of reaction products were determined spectrophotometrically. A general parallelism between the Liebermann – Burchard (sulphuric acid–acetic anhydride) and the Tshugaev reagent was confirmed except in the case of 5: 6 unsaturated 7-ketosteroids, which reacted to the latter reagent only. Arguments against currently suggested mechanisms for the Liebermann–Burchard reaction are presented, and a new mechanism for color production is postulated which involves ring cleavage. Experimental support is offered.

Introduction

Certain generalizations regarding the relationship between color production and steroid molecular structure have been suggested by Eck and Thomas (9), who determined the reactivity of a number of compounds to the sulphuric acid – acetic anhydride (Liebermann–Burchard) reagent (8, 11). They found that compounds having a double bond at the C_4 or C_5 position with or without an additional double bond or hydroxyl group, and without a ketone group at the C_3 or C_7 position, gave a positive Liebermann–Burchard color reaction. These workers additionally observed (10) that chemical antirachitic activation of sterols by means of such acidic "dehydrating" agents as sulphuric acid – acetic anhydride and zinc chloride – acetyl chloride (Tshugaev reagent) (17) was strictly correlative with color production; all compounds that yielded antirachitically active products gave a positive color test, while those which failed to yield active products did not give a positive test. Such factors as temperature, time, solvent, and proportion and character of reagents used were found to be important in both chemical activation and color production. Eck and Thomas observed a general parallelism as regards color-producing activity between the sulphuric acid – acetic anhydride reagent and the zinc chloride – acetyl chloride reagent.

During the course of collaborative work with Altschul (1) concerning the effect of several steroids on the rabbit, certain 5: 6 unsaturated 7-ketosteroids were found to give a positive color reaction with the Tshugaev reagent but no reaction with the Liebermann–Burchard reagent. In the discussion which follows the experimental section, a possible explanation for this exception to the general parallelism observed between these two reagents is offered, based on a new postulate for the mechanism of color production.

[1] *Manuscript received in original form May 29, 1950, and, as revised, November 24, 1950. Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask. This work was done during the tenure of a Life Insurance Medical Research Fund Student Fellowship by one of the authors (R.H.C.).*

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Experimental

Reagents

Zinc chloride reagent: a 20% solution (20 gm. per 100 ml.) of reagent zinc chloride in glacial acetic acid previously refluxed with and distilled from excess potassium permanganate. Acetyl chloride: reagent grade. Chloroform: refluxed with and distilled from excess anhydrous calcium chloride.

Colorimetric Estimation

Zinc chloride reagent (2 ml.) and acetyl chloride (1 ml.) were added to a solution of the steroid in chloroform (1 ml.) contained in a graduated glass-stoppered cylinder (10 ml.). The contents of the cylinder was mixed thoroughly and the resulting solution was heated in a water bath at 65°C. for six minutes to bring about color development; a reagent blank was heated simultaneously. After cooling, both solution and reagent blank were made up to volume (10 ml.) with chloroform.

The use of zinc chloride reagent without acetyl chloride resulted in much slower color development and less color stability. Acetyl chloride hence appeared to be both "sensitizer" and "stabilizer", a dual role suggested in part by Nield, Russell, and Zimmerli (14) from their investigations with an antimony trichloride–acetyl chloride reagent.

Absorption spectra of the color complexes produced with the steroids under investigation were determined over a wave length range of 320 to 600 mμ with the Beckman Model DU quartz spectrophotometer. The λ_{max} and ϵ_{max} values reported in Table I were obtained using steroid concentrations of 0.001%.

In addition to the λ_{max} seen in the table, compounds No. 1-5 showed another absorption maximum at 355 mμ, the value of ϵ_{max} being less than that observed at 525 mμ; compound No. 5, stigmasterol, also gave a further small

TABLE I

λ_{MAX} AND ϵ_{MAX} VALUES OF STEROID COLOR COMPLEXES

No.	Compound (common name)	Chemical name (as derivative of parent hydrocarbon)	λ_{max} (mμ)	ϵ_{max}
1	Cholesterol	Cholest-5-en-3(β)-ol	525	8700
2	Cholesteryl acetate	Cholest-5-en-3(β)-yl acetate	525	8880
3	Cholesterilene	Cholesta-3, 5-diene	525	13,100
4	Dicholesteryl ether	Cholest-5-en-3(β)-yl oxide	525	18,360
5	Stigmasterol	Stigmasta-5, 22-dien-3(β)-ol	525	5900
6	7-Dehydrocholesteryl benzoate	Cholesta-5, 7-dien-3(β)-yl benzoate	390	5850
7	Calciferol	Ergosta-5, 7, 10(19), 22-tetraene-3(β)-ol	395	8500
8	7-Ketocholesterol	Cholest-5-en-3(β)-ol-7-one	445	8360
9	7-Ketocholesteryl acetate	Cholest-5-en-7-on-3(β)-yl acetate	445	8480
10	7-Ketocholesterilene	Cholesta-3, 5-dien-7-one	445	7800

maximum at 400 mμ. Group No. 8-10, the 7-ketosteroids, gave another absorption maximum at 350 mμ, the ϵ_{max} value in this case being of approximately the same order of magnitude as that measured at 445 mμ. In both groups (No. 1-5 and No. 8-10), the ϵ_{max} at the absorption peak in the region of 350 mμ increased considerably when color development was carried out at a higher temperature or when the heating time was prolonged. Compounds 6 and 7, whose λ_{max} are both somewhat below 400 mμ, still absorbed sufficiently above this wave length to show a noticeable yellow coloration.

The compounds listed above as giving a positive color reaction with the zinc chloride–acetyl chloride reagent also gave a color test with the sulphuric acid–acetic anhydride reagent, except for the three 7-ketosteroids (No. 8-10), which gave no color. The color complexes developed with compounds 1-5 and 8-10 and the zinc chloride–acetyl chloride reagent were highly fluorescent. The fluorescence intensities of the color complexes with cholesterol and 7-ketocholesterol were investigated as a means of quantitative estimation (7).

Discussion

The known vitamers D all possess at the C_{19} position a methylene group formed by an activated (ultraviolet irradiation) rupture of ring B in the sterol precursor used in their preparation. Assuming that all antirachitic activation of sterols involves this same general phenomenon of ring rupture (and all existing evidence suggests that it does), the mechanism of chemical activation and hence color production might be postulated diagrammatically as shown in Fig. 1.

This postulate receives additional support from our observation that calciferol, with a ruptured ring B, gave an immediate color with either reagent, while color development with the other steroids was generally much slower. Color production was also immediate with 7-dehydrocholesteryl benzoate, a

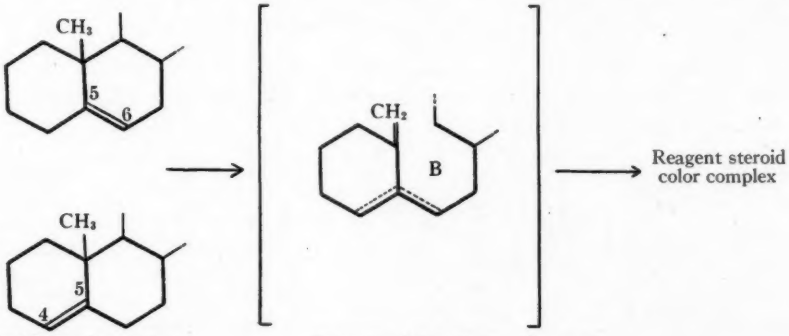

FIG. 1.

steroid possessing a conjugated (5: 6, 7: 8) diene system which renders ring B susceptible to cleavage by ultraviolet irradiation. Since antirachitic activation of sterols possessing a single unsaturation (4: 5 or 5: 6) is possible by chemical means but not by ultraviolet irradiation (10), it appears that chemical agents have the greater activating power. An almost immediate rupture of the more highly susceptible ring B of the 7-dehydrocholesteryl ester, with subsequent rapid color production, would hence be expected on the basis of the postulated mechanism.

Of interest in connection with the foregoing postulate is the observation of Eck and Thomas (10) that color change and antirachitic activation produced by the treatment of cholesterol with sulphuric acid–acetic anhydride were effected in less time when the reaction mixture was irradiated. This suggests a "reinforcement" of the chemical activating force.

The present postulate of ring rupture is substantiated, at least for cholesterol itself, by recent experiments of Raoul and coworkers (15). These investigators showed that cholesterol, in an ionizing medium such as acetyl chloride, was converted to vitamin D_3 through tachysterol as an intermediate, the per cent transformation varying inversely as the cholesterol concentration.

An explanation for the general unreactivity, towards the Liebermann–Burchard reagent, of compounds having a keto group in conjugation with a 4: 5 or 5: 6 unsaturation (i.e., at C_3 and C_7 respectively) may now be offered, based on the foregoing postulate. The stabilizing influence of an α, β-unsaturated ketone on an alicyclic, six-membered ring system may readily be established in an elementary fashion from its ultraviolet absorption spectrum (5) and optical rotatory power (2). It is suggested that this grouping in either of the previously mentioned positions in the steroid molecule sufficiently stabilizes the particular ring in which the unsaturation occurs that there is no longer sufficient activation of ring B to permit its rupture by the sulphuric acid–acetic anhydride reagent. That is, the 4: 5 or 5: 6 unsaturation is no longer an "activating" bond but rather a part of a stabilizing influence.

With these observations in mind a possible explanation for color production with the zinc chloride–acetyl chloride reagent and 7-ketocholesterol is offered diagrammatically in Fig. 2.

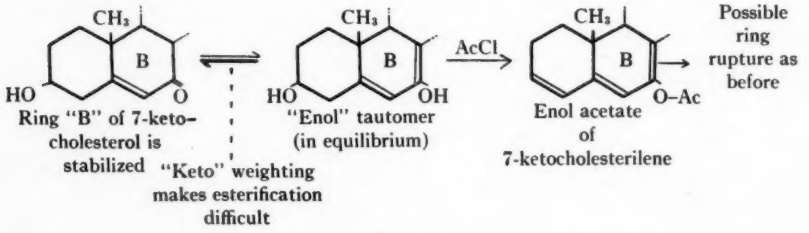

FIG. 2.

This acetylation of the enol form of 7-ketocholesterol at the C_7 position, together with the simultaneous introduction of an unsaturation in the 3:4 position, has been carried out experimentally by Spencer and Cox (16) using acetyl chloride. However, when 7-ketocholesteryl acetate was refluxed for eight hours with acetic anhydride, it was recovered unchanged, which suggests a possible explanation for the negative color test given with the Liebermann–Burchard reagent.

Although a number of mechanisms have been proposed for color production, none has previously considered ring rupture as a possible factor. The green color of the Liebermann–Burchard reaction has been attributed to the production of cholesteryl esters (4), but cholesteryl acid sulphate in the form of potassium and ammonium salts was found by Eck and Thomas (8) to be antirachitically inactive. Yoder (18) has proposed a mechanism involving dehydration of cholesterol to form dicholesteryl ether, with subsequent cleavage of the ether linkage to give one mole of cholesterilene and one mole of cholesterol, but Nath *et al.* (13) consider that dehydration to cholesterilene occurs directly. McKennis *et al.* (12) have interpreted the observation that on a molar basis the color intensity produced by dicholesteryl ether with the Liebermann–Burchard reagent is essentially twice that of cholesterol itself (a fact also noted with the Tshugaev reagent in the present investigation), as indirect support for Yoder's hypothesis of dicholesteryl ether cleavage by a cholesterol–cholesterilene route. If cholesterilene is a necessary intermediate in the production of color, however, it seems difficult to visualize its rapid formation from cholesteryl acetate by the splitting off of acetic acid in a medium of acetic anhydride—the medium, in effect, which is used to prepare the acetate of cholesterol. Such a phenomenon is even more difficult to accept as fundamental to color development when it is pointed out that both the free alcohol and its acetate show essentially the same rate of color development and the same color intensity.

On the basis of the postulate involving ring rupture, however, such reactions as ether formation and subsequent cleavage, direct dehydration, esterification, and sulphonation (which at the same time exert no appreciable negative effect on the normally activating unsaturation) might all occur to any extent without preventing the simultaneous production of color. Of further importance is the observation that the positive color test given with such compounds as cholestene (cholest-5-ene) and pseudocholestene (cholest-4-ene) (9) could readily be explained, even though these compounds afford no means of introducing the additional unsaturation necessary for the cholesterilene-type intermediates involved in the color mechanisms of other postulates. The twofold value of the ϵ_{max} of dicholesteryl ether would be expected on the basis of the two "B" rings per molecule (i.e., the unusual type of ether cleavage suggested by Yoder would not have to occur at all for color production on the basis of the ring rupture postulate). In addition, the relatively rapid color development noted with cholesterilene and the Tshugaev reagent (also observed by Eck and Thomas (10) with the Liebermann–Burchard reagent) might be attributed to

a further lowering of the stability threshold of ring B by the introduction of an additional unsaturation in the 3: 4 position, rather than to the suggested occurrence of cholesterilene as an intermediate in the process of color production.

Acknowledgments

The authors are indebted to Dr. A. D. Odell of Charles E. Frosst and Company, Montreal, for the gift of samples of 7-dehydrocholesteryl benzoate and calciferol. Acknowledgment is also made to Dr. H. B. Collier, Department of Biochemistry, University of Alberta, for helpful suggestions.

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STUDY OF NITRATION OF N,N′-DISUBSTITUTED HYDRAZINES[1]

By Jean P. Picard and Jean L. Boivin

Abstract

The nitration of N, N′-disubstituted hydrazines (RNH–NHR) by means of nitric acid – acetic anhydride mixtures has been found to yield, in most cases, the azo derivatives (RN=NR). For example, when R = CH_3, $(CH_3)_2(CN)C$, CH_3CO, or C_2H_5OCO, azo derivatives were formed. When R = HCO, nitrogen, carbon dioxide, and nitrogen oxides were evolved. An exception was observed with N, N′-dibenzoylhydrazine which, under the same conditions, yielded the N, N′-dinitro-N, N′-dibenzoylhydrazine.

Introduction

A recent survey of the literature has revealed the existence of four dinitroso derivatives of substituted hydrazines (3, 4, 12, 13), but the N, N′-dinitro derivatives of disubstituted hydrazines are still unknown. In the light of these facts it was of interest to investigate the formation of nitrate salts and nitro derivatives of some N, N′-disubstituted hydrazines. The substituted hydrazines prepared for the present study are listed in Table I.

TABLE I

Nitration products of disubstituted hydrazines

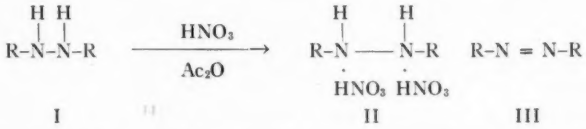
R–NH–NH–R (I)			R–N = N–R (III)		% HNO_3 in nitrates of I		% N in III	
R	M.p., °C.	Ref.	M.p., °C.	B.p. °C.	Calc.	Found	Calc.	Found
CH_3	168d[a]	5		102	67.7	67.0		
$(CH_3)_2(CN)C$	92–93	12	100–101		43.1	43.9	33.7	34.0
CH_3CO	140	9, 10, 11	104				24.5	24.1
C_6H_5	124	2	68					
HCO	160	8						
C_2H_5OCO	130–131	1	180d[b]	108–110 (15 mm.)				
C_6H_5CO	237–240	5, 7	118–119					

[a] *Isolated as the dihydrochloride.*
[b] *Azodicarbonamide, R = $CONH_2$.*

The N, N′-disubstituted hydrazines (I) were added to nitric acid – acetic anhydride mixture in the ratio of four moles of nitric acid per mole of hydrazo compound. By carrying out the reaction at low temperature, it was found that two of the disubstituted hydrazines used in this study (R = CH_3 and $(CH_3)_2$ C(CN), (Table I) yielded the dinitrate salt (II). As the reaction proceeded, the material went into solution, and simultaneous oxidation took place as seen from the formation of nitrous acid. When the reaction mixture was allowed to warm

[1] *Manuscript received September 11, 1950.*
Contribution from the Organic Section of the Canadian Armament Research and Development Establishment, Valcartier, Quebec.

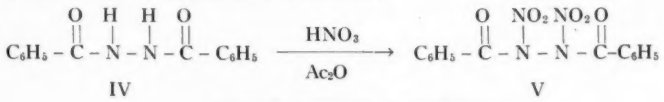
to room temperature, gases were evolved. In most cases the only materials isolated were nitrogen oxides and the azo derivatives (III) of the starting materials.



I II III

For example, N,N′-disubstituted hydrazines, where R = CH_3, C_6H_5, $(CH_3)_2C(CN)$, CH_3CO, or C_2H_5OCO, yielded the azo derivatives only, whereas N,N′-diformylhydrazine (I, R = HCO) was decomposed completely, giving gaseous products.

An exception was observed in the case of N, N′-dibenzoylhydrazine (IV) which, under the same conditions, yielded the N, N′-dinitro-N, N′-dibenzoylhydrazine (V), in admixture with its azo derivative (III, R = C_6H_5CO). This nitrated hydrazine was hydrolyzed by dilute alkalies to benzoic acid and nitrogen oxides. The ultraviolet absorption spectrum of V (Fig. 1), exhibits an absorption band at 2390Å which is characteristic of a secondary nitroamine, as was pointed out by Jones and Thorn (6).



IV V

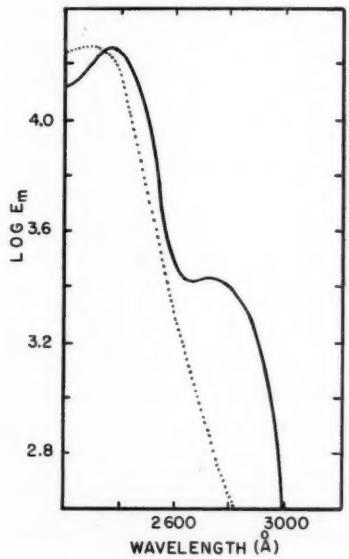


FIG. 1. *Ultraviolet absorption spectra.*
——— *N, N′-Dinitro-N, N′-dibenzoylhydrazine (ethanol).*
..... *1, 9-Diacetoxy-2, 4, 6, 8-tetranitro-2, 4, 6, 8-tetrazanonane (ethanol)* (7).

This behavior of N,N′-disubstituted hydrazines toward nitric acid – acetic anhydride mixture seems to be dominated by the basic character and reducing power of the hydrazine molecule itself, and appears to be dependent on the substituents employed.

The replacement of two hydrogens of hydrazine by benzoyl groups results in the formation of a weaker base. This effect is not surprising; it is analogous to the effect produced by the replacement of hydrogen in methyl amine by the benzoyl group, whereby a more easily nitrated secondary amine is formed.

Experimental[1]

The action of nitric acid – acetic anhydride mixture on N, N′-disubstituted hydrazines was studied at five different temperatures: –30°C., –20°C., –10°C., 0.5°C., and room temperature. Typical experimental procedures are given below.

Nitrations of N, N′-dimethylhydrazine (I, R = CH_3) and of N, N′-diformylhydrazine (I, R = HCO)

In a flask equipped to catch the gases formed in the reaction mixture were placed nitric acid (100%; 6.3 gm.; 0.1 mole) and acetic anhydride (30 ml.) previously mixed at –30°C. To this solution at –30°C. was added the dihydrochloride of I (3.3. gm.; 0.025 mole) and the mixture was allowed to warm to room temperature over a period of half an hour, during which time gases were evolved and condensed into a dry ice – acetone trap after they had been washed in alkaline solution. The reaction mixture was evaporated at 40°C. (1 mm.) and a trace of unidentified material remained in the flask. In the trap was present a low boiling liquid, b.p. 1–2°C., which was azomethane. When the reaction was held at –30°C., one could isolate from the mixture, by filtration through a sintered glass funnel, a white solid. This crystalline material was very hygroscopic, and after several washings with dry ether was identified as the dinitrate salt of N, N′-dimethylhydrazine. Calc. for $C_2H_{10}N_4O_6$: HNO_3, 67.7%. Found: HNO_3, 67.0%, after making a correction for the water content of the sample.

When N,N′-diformylhydrazine was treated in the same way as above, no nitrate salt could be obtained, and the gaseous product insoluble in alkaline solution was found to be nitrogen. After evaporation of the reaction mixture under reduced pressure, nothing remained in the flask.

Nitrations of Hydrazoisobutyronitrile (I, R = $(CH_3)_2(CN)C$) and Hydrazobenzene (I, R = C_6H_5)

To a solution of nitric acid (100%; 6.5 gm.; 0.1 mole), previously mixed at –30°C. with acetic anhydride (30 ml.), was added I (R = $(CH_3)_2(CN)C$) (4.15 gm.; 0.025 mole) in the solid form. During the addition the temperature was kept at –30°C., then the temperature was allowed to rise slowly. When

[1]*All melting points were corrected against reliable standards.*

the reaction mixture was held at –25°C. a white solid separated; this was filtered out by suction through a sintered glass funnel. This material, although quite hygroscopic, after several washings with dry ether was identified as a dinitrate salt. Calc. for $C_8H_{16}N_6O_6$: HNO_3, 43.1%. Found: HNO_3, 43.9%, after making a correction for the water content of the sample.

At –20°C. the crystalline compound began to dissolve and a green color appeared. At 5°C., solution was complete. After stirring at 25°C. for half an hour, the solution was poured into 100 gm. of cracked ice and water. The solid that separated out was filtered and washed free from acid with water, m.p. 95–100°C. Recrystallization from ethanol (50%) and from ether raised the melting point to 105°C. Yield 2.5 gm. (60%). Calc. for $C_8H_{14}N_4$: N, 33.7%. Found: N, 34.0%. This compound was identified as the azo derivative by a mixed melting point determination with an authentic sample.

When attempting the nitration of hydrazobenzene in the same manner, the only material isolated was azobenzene, which formed at temperatures as low as –30°C.

Nitration of N, N′-diacetylhydrazine (*I*, $R = CH_3CO$)

To the same proportions of acids as used in the former nitration was added an equivalent quantity of N, N′-diacetylhydrazine. When the reaction tem perature was kept at –30°C. for 15 min. a white powder could be isolated by drowning the reaction mixture in ice-water. If the reaction mixture was allowed to warm up, nitrogen and nitrogen oxides were evolved. This white solid material was soluble in ether, and melted at 104°C. with decomposition. A mixed melting point determination with a material prepared by the oxidation of N, N′-diacetylhydrazine with hypochlorous acid at low temperature showed no depression. Calc. for $C_4H_6N_2O_2$: N, 24.5%. Found: N, 24.1%.

Nitration of N, N′-dicarbethoxyhydrazine (*I*, $R = C_2H_5OCO$)

To a solution of nitric acid (100%; 7.0 gm.; 0.11 mole) in acetic anhydride 100 ml.) was added N, N′-dicarbethoxyhydrazine (8.8 gm.; 0.05 mole) at –30°C. The temperature of the colorless mixture was allowed to rise slowly to room temperature while the mixture was stirred. At 0°C. the solid dissolved with production of nitrous acid, and as the temperature rose the color deepened to red. After stirring at 25–30°C. for one hour, the red solution was poured into ice-water (300 gm.). A red oil separated out, ethyl azodicarboxylate, b.p. 108–110°C. (15 mm.). By treatment of this ester with ammonia, azodicarbonamide, a solid, was obtained, m.p. 180°C. with decomposition. Yield, 4.0 gm. (69%).

Nitration of N, N′-dibenzoylhydrazine (*I*, $R = C_6H_5CO$)

The same proportions as in the above described nitrations were used; the precipitated solid in ice-water was extracted with ether. The ethereal solution was washed thoroughly with dilute sodium hydroxide to get rid of the un-

changed starting material, dried over anhydrous sodium sulphate, and evaporated *in vacuo*. A white crystalline solid remained, m.p. 90–95°C. Recrystallizations from ethanol raised the melting point to 101.5°C. Yield, 2.5 gm. (31%). This compound gave a positive Franchimont test for nitramino groups and reacted with concentrated sulphuric acid, giving off nitrogen oxides. Calc. for $C_{14}H_{10}O_6N_4$: C, 50.9; H, 3.03; N, 16.9%. Found: C, 51.3; H, 3.15; N, 16.0%. From the mother liquor, another compound was obtained as a white powder which, after recrystallization from hot water, has a melting point of 118–119°C. This compound was shown by a mixed melting point determination with an authentic sample to be azodibenzoyl.

Hydrolysis of N, N'-dinitro-N, N'-dibenzoylhydrazine (*V*)

This compound (0.478 gm.), melting at 101.5°C., was boiled overnight in a solution of 1 gm. of sodium hydroxide in 50 ml. of ethanol (50%). The solution was evaporated to dryness under reduced pressure and the residue dissolved in water (20 ml.). The addition of an excess of concentrated hydrochloric acid to the solution precipitated a solid while nitrogen oxides (mainly NO_2) were evolved. The mixture was extracted with ether. The ethereal extract was washed with water, dried over anhydrous sodium sulphate and evaporated in a weighed platinum dish, leaving 0.375 gm. of solid melting at 120–121°C. After recrystallization from water this compound melted at 122°C. and was identified as benzoic acid. The yield of pure substance was 0.330 gm. or 94% if it is assumed that two moles of benzoic acid were produced from one mole of the material melting at 101.5°C.

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